SURFACE TENSION AND SONIC VELOCITY IN MIXTURES OF HYDROCARBON LIQUIDS

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PREFACE

The objective of this investigation was to develop a correlation between the sonic velocity and surface tension of hydrocarbon mixtures. An experimental apparatus was developed for measuring surface tensions. This apparatus is used to photograph bubbles of air suspended in a sample of liquid which is to be measured. The shape of the bubble is determined by the surface tension of the liquid. Basically the apparatus is a modification of the pendant drop method. This method has particular advantage where the surface tension of a volatile liquid is to be measured. Surface tension and density data were taken on 66 binary, 13 ternary and 4 quaternary mixtures.

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CHAPTER I

INTRODUCTION

Surface tension is an important property describing behavior of liquids when wetting, foaming, emulsification and droplet formation are encountered. The engineer needs to know or be able to estimate the surface tension of liquid mixtures for the solution of the following types of problems: the design of fractionators and absorbers, two-phase flow calculations for pipelines, and reservoir calculations.

Molecules located in the interior of a liquid are completely surrounded on all sides by other molecules. Over a long period of time the attractive forces on each molecule are uniform in all directions. Molecules located on the surface of the liquid are attracted inward and to each side by neighboring molecules. There are few molecules to provide an outward attractive force to balance the strong inward forces.

Molecules tend to move away from the surface faster than others move outward to take their place, due to the strong inward forces. Hence, the surface tends to contract until the maximum possible number of molecules are in the interior of the liquid. In order to increase the surface of the liquid, work must be done on the liquid. This is the work needed to bring molecules from the interior to the surface of the liquid against the strong inward forces.

Since the surface contracts spontaneously, a free energy must be associated with the surface. The free energy of the surface must be the work done to change the surface area. The surface free energy is usually expressed in terms of a hypothetical tension acting in all directions parallel to the surface. This tension, known as the surface tension, is a mathematical convenience and equals the free energy of the surface.

For multicomponent systems the surface free energy can be reduced spontaneously in a way other than by reducing the surface area of the liquid. Components of lower surface tension are adsorbed at the surface thereby lowering the surface tension of the mixture. This phenomena is usually referred to as the Gibbs adsorption, and plays an important role in the theory of surface tension of mixtures.

The investigation of the velocity of propagation of sound through a fluid provides a convenient method for studying the intermolecular forces between molecules. The compressibility of a fluid is directly related to the sonic velocity through the well known relationship (27).

$$\hat{\gamma}\beta_s = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{-\hat{\gamma}}{\rho\hat{U}^2} \tag{1}$$

β_s is the adiabatic compressibility. $\hat{\gamma}$ is the heat capacity ratio. V is the molar volume. ρ is the density, $\hat{U}$ is the sonic velocity. P is the pressure, and the subscript T denotes constant temperature.

The objective of this study is to determine the relationship between the sonic velocity and surface tension in mixtures of hydrocarbon liquids. Several relationships between sonic velocity and surface tension (3,5,27, and 36) have already been developed for pure components. Some of these relationships have been used to correlate sonic velocity and surface tension for liquid mixtures.

CHAPTER II

LITERATURE SURVEY

The Relationship Between Surface Tension and Sonic Velocity

The relationship between sonic velocity and surface tension has been investigated by several authors. Most of the work has been limited to pure components. In general, the relationships between sonic velocity and surface tensions have been largely empirical in nature.

One of the most interesting relationships is that of Cornelissen, Waterman, and Waterman (5). The following simple linear relationship between sonic velocity and surface tension was proposed.

$$\sigma_{20} = 0.0354\ \hat{U}_{20} - 20.6 \tag{2}$$

σ_{20} is the surface tension in dynes/cm. at 20°C. $\hat{U}_{20}$ is the sonic velocity in m/sec. at 20°C. This empirical relationship was obtained from data on pure saturated hydrocarbons (n-alkanes, branched alkanes, and monocyclic naphthenes) and saturated mineral oil fractions, which have a very low content of aromatics (less than 0.5 aromatic rings per molecule). This relationship applies only at 20°C. Cornelissen et al. (5) have proposed that other relationships similar to equation 2 apply at other temperatures. The only differences between the equations are the constants which are a function of temperature.

These authors (5) have also suggested that the surface tension of a single pure component is related to its sonic velocity in the following manner:

$$\sigma = B\hat{U} + C \tag{3}$$

σ is the surface tension. $\hat{U}$ is the sonic velocity. B and C are numerical constants. Equation 2 is very similar to equation 3. Equation 2 applies to all compounds at only a temperature of 20°C. Equation 3 applies only to one compound but applies over a larger range of temperature. For example:

$$\text{n-heptane} : \sigma = 0.0236\ \hat{U} - 7.1 \tag{4}$$

$$\text{n-octane} : \sigma = 0.0224\ \hat{U} - 5.1 \tag{5}$$

The relationships presented in equations 2 through 5 demonstrate that the surface tension can be determined from only one physical property, the sonic velocity. The relationships are accurate only for saturated hydrocarbons. Equation 2 fits data for these types of compounds within an average of ± 1 - 2%.

The surface tension of low molecular weight n-olefins may deviate as much as -5% from equation 2. As the molecular weight of the olefins increases the error decreases, indicating a decrease in the influence of the double bond. The values of the predicted surface tension for n-olefins are always less than experimental values.

The surface tension of aromatic compounds may deviate from equation 2 by as much as -10%. These deviations indicate that, while these relationships are very interesting for saturated hydrocarbons, they cannot be relied upon to yield accurate results for other types of compounds.

Auerbach (3) has suggested another empirical relationship between surface tension and sonic velocity. Auerbach observed that when log σ/ρ was plotted against the logarithm of the velocity of sound a straight line resulted. From this he deduced the relationship:

$$\sigma/\rho = C\hat{U}^{3/2} \tag{6}$$

C is an arbitrary constant. Auerbach suggests a value for C of 6.3×10^{-4} when σ is in dyne/cm., ρ is in gm/cm^3 and $\hat{U}^2$ is in m/sec.

Equation 6 was developed from data on several types of organic liquids as well as inorganic liquids at several temperatures. While equation 6 was developed for pure components, Auerbach (3) has suggested that it might also apply to mixtures of liquids, if the effect of adsorption at the interface was small.

Recently, Kolwalska, E., W. Kolwalski, and Slaczka (26) used equation 6 to correlate the surface tension of binary mixtures as a function of sonic velocity over a range of temperatures from 20-60°C. The systems used in this study were carbon tetrachloride-benzene, n-butyl alcohol-p-nitrophenol, aqueous ethyl alcohol, aqueous sulfuric acid, and aqueous phosphoric acid. These authors showed that equation 6 applied under the following conditions: (1) for nonpolar compounds, (2) for associated systems where the temperature coefficient of the sonic velocity is negative, and (3) for strong electrolytes.

Considering the wide range of applicability of equation 6, this type of a relationship should be very useful in correlating the surface tension of hydrocarbon mixtures

Kudriavtsev (27) and Nozdrev (35) have proposed correlations for sonic velocity in liquids based upon "thermodynamic relationships which exist between various physical characteristics" of liquids. These relationships rely on several postulates which cannot be fully justified theoretically. To develop the equations presented by these authors we start with equation 1:

$$-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{\hat{\gamma}}{\rho\hat{U}^2} \tag{7}$$

or

$$\hat{U}^2 = -\frac{\hat{\gamma}V^2}{M}\left(\frac{\partial P}{\partial V}\right)_T \tag{8}$$

M is the molecular weight. To evaluate equation 8 an equation of state for liquids must be developed. From statistical thermodynamics (20), one expression for the free energy of a liquid is:

$$F = -RT \ln \frac{v(2\pi mkT)^{3/2}}{h^3} + \Phi \tag{9}$$

F is the Helmholtz free energy. R is the gas constant. T is the temperature. v is the volume per molecule, m is the mass per molecule. h is Plank's constant. k is Boltzman's constant. Φ is the potential energy per mole of the fluid arising from the intermolecular forces.

Equation 9 essentially is the free energy of an ideal gas to which a term Φ has been added. The free energy of an ideal gas is arrived at through considerations of only the translational energy of the molecules. For equation 9 the attractive forces between molecules of the liquid are accounted for by simply adding a potential energy Φ to the free energy. Therefore, the equation of state can be deduced from the thermodynamic relationship:

$$P = -\left(\frac{\partial F}{\partial V}\right)_T \tag{10}$$

V is the volume per mole. Differentiating equation 9 and substituting into equation 10 yields:

$$P = \frac{RT}{V} - \left(\frac{\partial \Phi}{\partial V}\right)_T \tag{11}$$

Differentiating equation 11 and substituting into equation 8 yields:

$$\hat{U}^2 = \frac{\hat{\gamma}RT}{M} + \frac{\hat{\gamma}V^2}{M}\left(\frac{\partial^2 \Phi}{\partial V^2}\right)_T \tag{12}$$

At this point, an assumption about the nature of the potential energy of the fluid is introduced. The potential energy between two molecules can be approximately represented by the Lennard-Jones equation.

$$\Phi(\ell) = \frac{B_1}{\ell^{b_1}} - \frac{D_1}{\ell^{d_1}} \tag{13}$$

B_1, D_1, b_1, and d_1 are constants. ℓ is the intermolecular distance. $\Phi(\ell)$ is the intermolecular potential. Equation 13 can thus be expressed in terms of volume.

$$\Phi = \frac{B}{V^b} - \frac{D}{V^d} \tag{14}$$

b, d, B, and D are defined by the following:

$b = b_1/3$

$d = d_1/3$

B = constant

D = constant

The exponent b is a function of the attractive forces and must be equal to two. The exponent d is a function of the repulsive forces. A value for d cannot, as yet, definitely be assigned. d is usually considered to be about four. The quantities B and D in equation 14 are functions of temperature. At constant temperature they are characteristic for the specified liquid. As stated previously, equation 14 is valid only for the interaction of two molecules. The assumption is made that the potential energy of the liquid has the same form as equation 14. This assumption is definitely an approximation, but can provide a convenient interpolation formula if we allow the constants B and D to remain arbitrary. Differentiating equation 14 twice and substituting into equation 12 yields

$$\frac{M\hat{U}^2}{\hat{\gamma}} = RT - d(d+1)DV^{-d} + b(b+1)BV^{-b} \tag{15}$$

B and D must satisfy the following conditions:

$$PV = RT + bBV^{-b} - dDV^{-d} \tag{16}$$

$$\Phi_o = BV^{-b} - DV^{-d} \tag{17}$$

Φ_o is the energy required to move one mole of liquid from the liquid phase to the gas phase under equilibrium conditions. Solving equations 16 and 17 simultaneously we have

$$B = \frac{V^b}{b-d}\left[PV-RT-d\Phi_o\right] \tag{18}$$

$$D = \frac{V^d}{b-d}\left[PV-RT-b\Phi_o\right] \tag{19}$$

Substituting equations 18 and 19 into 15 gives:

$$\frac{M\hat{U}^2}{\hat{Y}} = bd\Phi_o + PV(b+d+1) - RT(b+d) \tag{20}$$

The above equation was presented by Nozdrev (35). He suggested that Φ_o could be evaluated from the latent heat of vaporization i.e. $\Phi_o = \lambda - RT$ where λ is the heat of vaporization. As pointed out by Kudriavtsev (27), this does not yield results which are consistent with modern concepts. When the heat of vaporization is used b must equal one to fit the data.

A better method of evaluating Φ_o can be obtained from the equation presented by Rutgers (43). To derive these equations, a reversible process is considered in which the surface area of the liquid is increased. In such a process the heat added to the system is:

$$\delta_{Rev} = T\,ds \tag{21}$$

δ_{Rev} is the reversible heat and s is the entropy.

$$T\,ds = du + \delta_w \tag{22}$$

u is the internal energy. δ_w is the work done by the system. To evaluate the work done by the system we examine a typical process in which a liquid film is stretched in a wire frame, as shown in Figure 1. The force exerted by the liquid on the wire of length l is $2\,\sigma\,l$ (the factor 2 accounts for the fact that there are two liquid surfaces on the film i.e., the upper and lower surface). Hence, the work done by the film to extend the surface is:

$$\delta_w = -\sigma dA \tag{23}$$

A is the total surface of the liquid. Substitute equation 22 into 23:

$$du = T\,ds + \sigma dA \tag{24}$$

The change in free energy can be determined by the thermodynamic relationship:

$$F = u - Ts \tag{25}$$

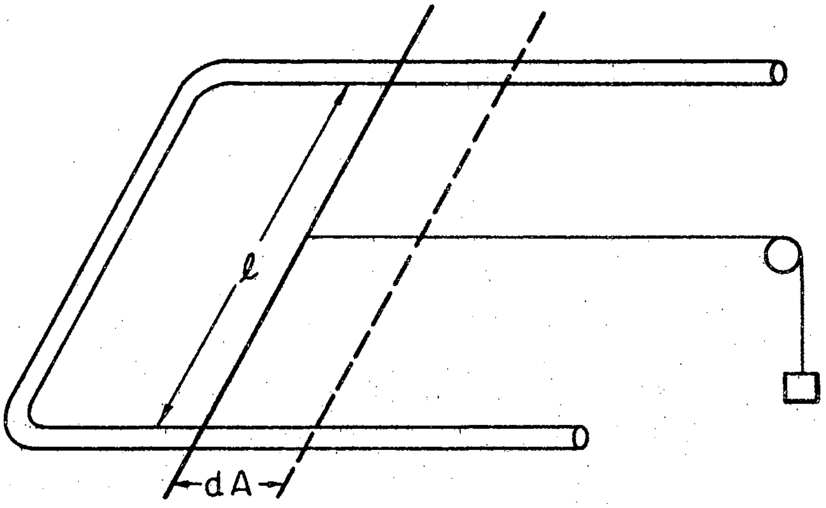

Figure 1. Surface Tension in a Stretched Liquid Film

or

$$dF = du - Tds - sdT \tag{26}$$

Substitute 24 into 26

$$dF = -sdT + \sigma dA \tag{27}$$

Green's theorem can be applied since dF is an exact differential

$$-\left(\frac{\partial s}{\partial A}\right)_T = \left(\frac{\partial \sigma}{\partial T}\right)_A \tag{28}$$

From equation 27

$$\left(\frac{\partial F}{\partial A}\right)_T = \sigma \tag{29}$$

Differentiating equation 25 at constant temperature.

$$\left(\frac{\partial F}{\partial A}\right)_T = \left(\frac{\partial u}{\partial A}\right)_T + T\left(\frac{\partial \sigma}{\partial T}\right)_A \tag{30}$$

Substitute equations 28 and 27 into 30

$$\left(\frac{\partial u}{\partial A}\right)_T = \sigma - T\left(\frac{\partial \sigma}{\partial T}\right)_A \tag{31}$$

Therefore the expression $\sigma - T\left(\frac{\partial \sigma}{\partial T}\right)_A$ represents the increase in energy of the surface film required to change the surface area isothermally.

With these relationships surface tension can be related to the energy required to remove a molecule from the liquid into the vapor phase, Φ_0. Consider an idealized vapor-liquid transformation that is infinitely sharp. The assumption is made that the interaction between molecules occupying symmetrical positions with respect to the phase boundary are attracted towards the interior of the liquid with equal force. Therefore, the work required to bring a molecule to the surface must equal half of the work to bring the molecule into the vapor phase. On the other hand the energy required to increase the surface area to accommodate the evaporating molecule is equal to

$$\omega\left(\frac{\partial u}{\partial A}\right)_T = \omega\left[\sigma - T\left(\frac{\partial \sigma}{\partial T}\right)_A\right] \qquad (32)$$

ω is the surface area of one molecule. Therefore

$$\frac{1}{2}\,\frac{\Phi_o}{N} = \omega\left[\sigma - T\left(\frac{\partial \sigma}{\partial T}\right)_A\right] \qquad (33)$$

N is Avogadro's number. If the molecule does not depart seriously from spherical symmetry, then the surface area can be estimated by assuming that each molecule occupies a cube of the size V/N, with edges $(V/N)^{1/3}$ long. Hence

$$\omega = \left(\frac{V}{N}\right)^{2/3} \qquad (34)$$

Substitute 34 into 33

$$\Phi_o = 2\left[\sigma - T\left(\frac{\partial \sigma}{\partial T}\right)_A\right] V^{2/3} N^{1/3} \qquad (35)$$

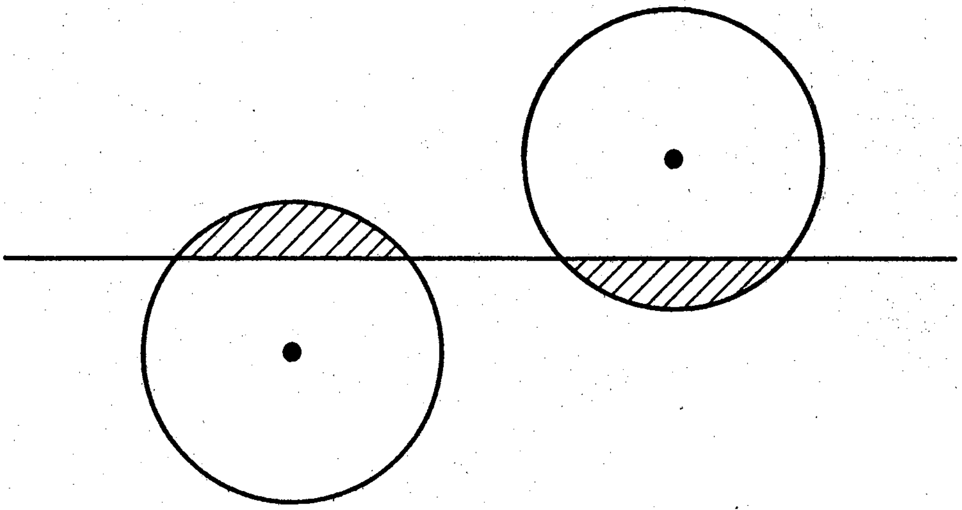

Figure 2. Molecules Evaporating Through the Surface Phase

Now substitute equation 35 into 20

$$\frac{M\hat{U}^2}{\hat{\gamma}} = 2bd\left[\sigma - T\left(\frac{\partial\sigma}{\partial T}\right)_A\right]V^{2/3}N^{1/3} + PV(b+d+1)-RT(b+d) \tag{36}$$

If we assume that

$$PV \cong RT \tag{37}$$

Also assume that $T\left(\frac{\partial\sigma}{\partial T}\right)_A$ is negligible. Therefore, equation 36 can be written as

$$\hat{U}^2 = (2bd\hat{\gamma}N^{1/3})\frac{\sigma}{M^{1/3}\rho^{2/3}} + \frac{\hat{\gamma}RT}{M} \tag{38}$$

This is the equation derived by Kudriatsev (27). In order to obtain this equation, a questionable assumption was made. $T\left(\frac{\partial\sigma}{\partial T}\right)_A$ is not negligible if liquids of low surface tensions, such as hydrocarbons, are to be considered. For example, benzene at 25°C has the following properties:

$$\sigma = 28.18 \text{ dyne/cm} \tag{39}$$

$$-T\left(\frac{\partial\sigma}{\partial T}\right)_A = 22.05 \text{ dyne/cm} \tag{40}$$

Therefore equation 36 should be used in preference to equation 38.

Jacobson (22,23,24,25) has extensively investigated the physical properties of liquids as a function of the distance between the surfaces of the molecules or the intermolecular free length. He suggested that physical properties such as compressibility, surface tension, and viscosity can be related empirically to the intermolecular free length in the following manner

$$j = CL^b \tag{41}$$

j is a physical property. L is the intermolecular free length. C and b are constants which are a function of temperature only. L can be estimated from

$$L = \frac{2(V-V_o)}{(\hat{Y})} \tag{42}$$

V_o is the molecular volume at absolute zero. $\hat{Y}$ is the total surface area per mole. For spherical molecules $\hat{Y}$ can be determined from

$$\hat{Y} = (36\pi\ N\ V_o^2)^{1/3} \tag{43}$$

for nonspherical molecules equation 43 can be written as

$$\hat{Y} = f(36\pi\ N\ V_o^2)^{1/3} \tag{44}$$

f is the shape factor to account for nonspherical molecules. V_o can be estimated by using Sugden's (48) formula to extrapolate the volume to absolute zero.

$$V = V_o\left(1-\frac{T}{T_c}\right)^{0.3} \tag{45}$$

Equation 42 is only an approximation. The true intermolecular free length has to be based on a given type of packing of molecules and form of the molecules. For a hexagonal packing of spherical molecules the free length is according to Eyring's theory

$$L_{Hex} = \left(\frac{\sqrt{2}}{N}\right)^{1/3} (V_T{}^{1/3} - V_o{}^{1/3}) \tag{46}$$

The exact intermolecular free length does not need to be obtained if an empirical correlation such as equation 41 is to be developed. Jacobson (24) found that free length calculated from equation 46 did not correlate physical properties any better than those calculated from equation 42.

Equation 42 has an important advantage over an exact treatment in that it can be easily applied to mixtures, whereas exact methods cannot. For binary mixtures, L can be calculated from

$$L = \frac{2\left[\frac{1}{\rho} - \left\{\frac{W_1 V_{o1}}{M_1} + \frac{W_2 V_{o2}}{M_2}\right\}\right]}{\frac{W_1 \hat{Y}_1}{M_1} + \frac{W_2 \hat{Y}_2}{M_2}} \tag{47}$$

W_i is the weight fraction. The subscripts 1 and 2 refer to components 1 and 2, and ρ is the density of the mixture. Jacobson (24) using equation 41 and the free length calculated from equation 42 has correlated the adiabatic compressibility of liquids and their mixtures at temperatures close to room temperature.

$$\beta_s = C\ L^2 \tag{48}$$

C is a constant which is a function of temperature. Using equation 1, equation 48 can be used to determine sonic velocities,

$$\hat{U} L^{1/2} \rho = C \qquad (49)$$

The numerical values of C as a function of temperature are presented in Table I.

Jacobson (25) has also shown that equation 41 can be used to correlate the surface tension of pure liquids. Using this approach he obtained:

$$\sigma = C' \; L^{-3/2} \qquad (50)$$

C′ is a constant. The numerical values for C′ obtained by Jacobson are presented in Table II as a function of temperature.

Jacobson has shown that equation 50 does not apply directly to mixtures because the surface layer of a liquid does not have the same composition as the bulk fluid. When the surface composition is known, the intermolecular free length can be computed from equation 47, and the surface tension can be computed from equation 50. The surface composition cannot be measured because of the small thickness of this layer. This composition must be computed from the known values of surface tension as a function of composition.

If equations 48 and 50 are combined, a relationship between surface tension and compressibility (or sonic velocity) can be developed

$$\beta_s \sigma^{4/3} = \text{Constant} \qquad (51)$$

TABLE I

JACOBSON'S FORMULA AND CONSTANTS FOR COMPUTING SONIC VELOCITIES IN PURE LIQUIDS AND MIXTURES

$\hat{U}L^{\frac{1}{2}} = C$

$\hat{U}$ in M/sec.

L in cm.

ρ in gm/cm.

T° C	C
0	588
10	604
20	618
25	625
30	631
40	642
50	652

TABLE II

JACOBSON'S FORMULA AND CONSTANTS FOR COMPUTING SURFACE TENSIONS IN PURE COMPONENTS

$$\sigma = C' L^{-3/2}$$

σ in dyne/cm.

L in cm.

T°C	-log C′
0	11.032
10	11.008
20	10.986
25	10.976
30	10.966
40	10.948
50	10.932

This is a well known relationship, cf. Partington (36). As can be seen, this relationship should apply only over a moderate temperature range. In addition, this relationship should not apply to mixtures because of Gibbs adsorption at the surface layer.

Surface Tension of Mixtures

Several authors have investigated the thermodynamics of the surface layer for mixtures (11,12,17,24,44,45). By using the relationships discussed by Erikson (12), Sprow and Prausnitz (45), have derived a method which will allow the computation of the surface tension and surface composition of liquid mixtures. This method was derived by considering the change in chemical potential for the following process in a multicomponent mixture.

process	change in chemical potential	
take a quantity of liquid from the bulk phase and separate into pure components	$\mu_i - \mu_i^M = -RT \ln a_i$	(52)
form the pure surface layers from the pure components	$\mu_i^S - \mu_i = \sigma_i \Omega_i$	(53)
mix the pure component surface phases to form the equilibrium surface phase	$\mu_i^{MS} - \mu_i^S = RT \ln a_i^S - \bar{\Omega}_i \sigma^M$	(54)
add the surface phase to the bulk phase	$\mu_i^{MS} - \mu_i^{MS} = 0$	(55)

μ_i is the chemical potential of species i. a_i is the activity of species i. The superscript M refers to the mixture. The superscript S refers to the surface phase. Ω is the surface area per mole of species, i.e., in terms of the previously defined ω.

$$\Omega = N\omega \tag{56}$$

The overall change for the above process is

$$\mu_i^{MS} - \mu_i^{M} = 0 \tag{57}$$

σ^M is the surface tension of the mixture. $\bar{\Omega}_i$ is the partial molar surface area of species i. Hence:

$$\sigma^M = \frac{\Omega_i}{\bar{\Omega}_i}\,\sigma_i + \frac{RT}{\bar{\Omega}_i}\,\ln\frac{a_i^S}{a_i} \tag{58}$$

The surface tension of mixtures can be estimated from equation 58 by first assuming that;

$$\bar{\Omega}_i = \Omega_i \tag{59}$$

For most liquids this assumption can be used without any appreciable loss of accuracy. Introducing the activity coefficients gives:

$$a_i = \gamma_i X_i \tag{60}$$

$$a_i^S = \gamma_i^S X_i^S \tag{61}$$

γ_i is the activity coefficient. X_i is the mole fraction. Therefore:

$$\sigma^M = \sigma_i + \frac{RT}{\Omega_i}\,\ln\frac{\gamma_i^S X_i^S}{\gamma_i X_i} \tag{62}$$

The bulk phase activity coefficient γ_i can be evaluated in the usual manner from vapor-liquid data. The surface area Ω_i can be estimated from equations 34 and 56, i.e.,

$$\Omega_i = V^{2/3}N^{1/3} \tag{63}$$

If the mixture is relatively simple (dispersion forces predominate in the surface layer and the molecules are of similar size), the surface can be treated as a regular solution. The activity coefficients of the surface phase can be determined by the method presented by Sprow and Prausnitz (44):

$$RT \ln \gamma_i^S = \Omega_i(\delta_i^s - \overline{\delta}^s)^2 \tag{64}$$

$$\overline{\delta}^s = \Sigma\theta_i\delta_i^s \tag{65}$$

$$\theta_i = \frac{x_i^s\Omega_i}{\Sigma x_j^s\Omega_j} \tag{66}$$

θ_i is the surface area fraction of component i, and δ_i^s is the square root of the surface cohesive energy density of component i. The term δ_i^s can be estimated from the relationship presented by Eckert and Prausnitz (11).

$$(\delta_i^s)^2 = \frac{\Delta h_i^{vap} + (h_i^{id} - h_i^{sat}) - (RT - P_i^{sat}V_i)}{\Omega_i} - \sigma_i + T\left(\frac{\partial\sigma_i}{\partial T}\right) \tag{67}$$

Equations 58 through 67 can be used to compute the surface tension of a liquid mixture by a trial and error procedure. The value of the surface tension can be assumed, and the composition of the surface X_i^s calculated. The correct value of σ^M is assumed when the following relationship is satisfied

$$\Sigma X_i^s = 1.0 \tag{68}$$

Once the correct value of σ^M has been determined, the correct value of X_i^s is also obtained.

This method has been tested by Sprow and Prausnitz (45) for cryogenic mixtures and hydrocarbon mixtures. The method allowed the computation of mixture surface tensions which are within experimental error.

If the solution is ideal, i.e., the activity coefficients are equal to unity and if the surface areas of each component are equal, then equation 62 will reduce to the Guggenheim (17) equation

$$e^{\frac{-\sigma^M \Omega}{RT}} = \Sigma X_i e^{\frac{-\sigma_i \Omega}{RT}} \tag{69}$$

Eberhart (10) has proposed an approximate method for correlating the effect of composition on the surface tension for binary mixtures. He assumed that the surface tension was a linear function of the surface mole fraction.

$$\sigma^M = X_1^s \sigma_1 + X_2^s \sigma_2 \tag{70}$$

In order to relate the surface composition to the bulk composition an equilibrium constant was defined

$$\hat{K}_i = \frac{a_i^s}{a_i} \tag{71}$$

$\hat{K}_i$ is a type of distribution constant which is a function of temperature only. Next a separation factor is defined such that

$$\hat{S} = \frac{\hat{K}_1}{\hat{K}_2} = \frac{a_1^s/a_2^s}{a_1/a_2} \tag{72}$$

$\hat{S}$ is the separation factor which is again only a function of temperature. If the liquid mixture is ideal, the activities can be replaced with mole fractions.

$$\hat{S} = \frac{X_1^s/X_2^s}{X_1/X_2} \tag{73}$$

Equations 70 and 73, along with the condition that the summation of the mole fraction must equal unity, yields:

$$\sigma = \frac{\hat{S}X_1\sigma_1 + X_2\sigma_2}{\hat{S}X_1 + X_2} \tag{74}$$

Equation 74 is largely untested. Indications are that, while this method can be used to fit many binary liquid mixtures, many cannot be fitted by this equation. The systems which could not be fitted are composed of components whose properties would not be described as similar. Therefore, the conclusion is made that for unlike compounds $\hat{S}$ is a function of composition.

Weinaug and Katz (52) developed a method for estimating the surface tension of mixtures of known composition at high pressures.

$$\sigma^M = \left[\sum_{i=1}^{N} \hat{P}_i \left(\frac{\rho_L X_i}{M_L} - \frac{\rho_V Y_i}{M_V}\right)\right]^4 \tag{75}$$

σ^M is the surface tension of the mixture. $\hat{P}_i$ is the parachor for component i. ρ_L is the density of the liquid mixture. ρ_V is the vapor density of the mixtures. M_L is the molecular weight of the liquid. M_V is the molecular weight of the vapor. X_i is the mole fraction of component i in the liquid and Y_i is the mole fraction of component i in the vapor. The parachor is calculated by use of Sugden's (48) equation

$$\hat{P} = \frac{\sigma^{1/4} M}{\rho_L - \rho_V} \tag{76}$$

Deam (9) has studied the methane-nonane and the methane-butane-decane systems. His data showed that the Weinaug-Katz equation fitted experimental results with about an absolute deviation of 4-8%.

Sonic Velocity

Nomoto (31,32,33,34) has studied the variation of the velocity of sound with composition. His methods were based primarily on the previous work of Rao (39) and Wada (51). These methods are largely empirical, but they are probably the most accurate for estimating the velocity of sound in a mixture.

Rao has suggested that the ratio of the temperature coefficient of the velocity of sound to the temperature coefficient of the volume is equal to -3

$$\frac{\frac{1}{\hat{U}}\frac{d\hat{U}}{dT}}{\frac{1}{V}\frac{dV}{dT}} = -3 \tag{77}$$

This rule was postulated strictly on the basis of experimental data. However, Nozdrev (35) has shown that equation 77 does have an approximate theoretical basis. He has shown that by the use of equation 15

$$\frac{\frac{1}{\hat{U}}\frac{d\hat{U}}{dT}}{\frac{1}{V}\frac{dV}{dT}} = -\frac{b}{2} \tag{78}$$

Hence, Rao's constant is related directly to the exponent in equation 14 which represents the repulsive term of the potential energy function.

From equation 77 the following equation can be developed:

$$\overline{R}_A = (M/\rho)\hat{U}^{1/3} \tag{79}$$

$\overline{R}_A$ is the so called "molecular sonic velocity" which is a function of the component and is independent of temperature. Nomoto (32) has shown that for many mixtures of simple liquids the molecular sonic velocity of the mixture is a linear function of molar composition.

Another method presented by Nomoto uses the so-called Wada Molecular compressibility. Wada (51) defined the molecular compressibility as:

$$\bar{W} = (M/\rho)\beta_s^{-1/7} \tag{80}$$

$\bar{W}$ is the molecular compressibility. Equation 1 can be substituted into equation 80 to give

$$\bar{W} = M^{1/7}\,\bar{R}_A^{6/7} \tag{81}$$

$\bar{W}$ is also a function only of the compound and is independent of temperature. Nomoto (32) has shown that the molecular compressibility is a linear function of mole fraction for many mixtures of both simple and complex liquids.

Before either equations 79 or 80 can be used to predict sonic velocities for mixtures the relationship between density and composition must be known. Thus, Nomoto (34) has suggested a third method based on Rao's molecular sonic velocity. He assumed that the molecular volume is a linear function of the molecular composition. With this assumption he derived the following equation for binary mixtures:

$$\hat{U} = \left[\frac{X_1\,\bar{R}_{A1} + X_2\,\bar{R}_{A2}}{X_1 V_1 + X_2 V_2}\right]^3 \tag{82}$$

$\bar{R}_{Ai}$ is the molecular sonic velocity of the i^th species. All three of the methods presented by Nomoto were tested using literature data for hydrocarbon mixtures. The results of these calculations are presented in Appendix A. Each method gives approximately the same results. However, the method using Wada's molecular compressibility does fit the data better from an overall standpoint.

Experimental Methods of Measuring Surface Tension

Many methods of measuring surface tension are available. The most commonly used methods depend on observing the behavior of the fluid in a capillary tube, the tension required to pull a wire ring out of the liquid surface, the volume or weight of drops falling from a vertical tube, or the maximum pressure required to form a bubble. Most of the above methods are very seriously limited by the fact that either the methods are not completely static or, as in the case of the capillary method, they depend on the contact angle with the solid phase being zero.

One of the most outstanding methods is the pendant drop method suggested by Andreas, Hauser, and Tucker (3). In this method a drop is suspended from the tip of a vertical tube and photographed. The photograph can be precisely measured. Since the drop is a surface of revolution, the drop shape can be computed exactly from known mathematical relationships.

Andreas, et al. (3) have suggested the "selected plane" method of measuring the drop photograph. In this method the diameter at the equator of the drop, d_e, is measured as shown in Figure 3. Also the diameter at the selected plane, d_s, is measured. The selected plane is located one equatorial diameter from the bottom of the drop.

The shape of the drop can be determined by considering a pressure balance across the surface of the drop. The effect of the radii of curvature on the pressure was presented by Adams (1).

$$P = \sigma\left(\frac{1}{r} + \frac{1}{r'}\right) \tag{83}$$

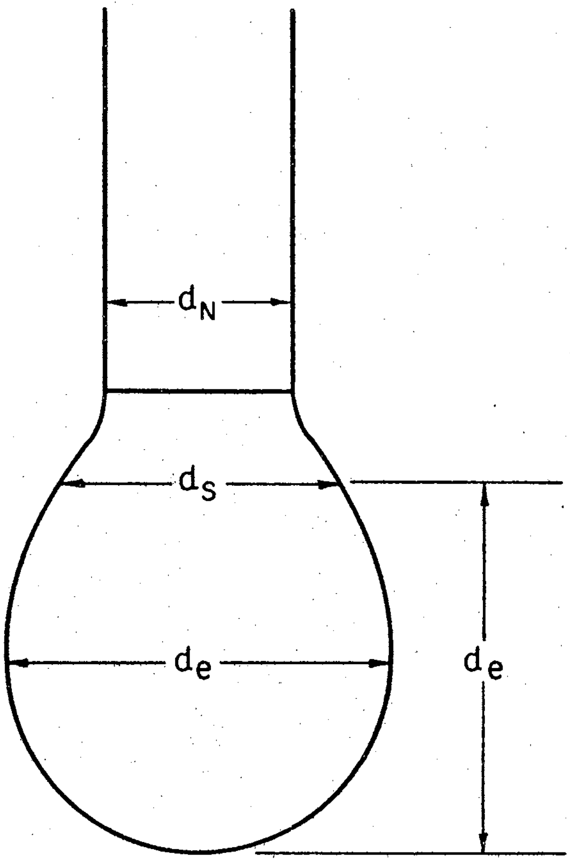

Figure 3. Selected Plane Method of Measuring Surface Tension

r and r′ are the two principal radii of curvature. P is the pressure due to the curvature of the surface. The pressure at any point due to the curvature of the surface, when the bottom of the drop is located at the origin of the coordinate system, is as follows:

$$P = \frac{2\sigma}{r_o} - g(\rho_L - \rho_V)z \tag{84}$$

r_o is the radius of curvature at the origin of the drop. g is the local acceleration of gravity. z is the vertical coordinate. $(\rho_L - \rho_V)$ is the difference between the density of the liquid and vapor phases. Combining equations 83 and 84 yields

$$\sigma\left(\frac{1}{r} + \frac{1}{r'}\right) = \frac{2\sigma}{r_o} - g(\rho_L - \rho_V)z \tag{85}$$

The radii of curvature can be eliminated by using the following relationship:

$$r' = \frac{\left[1 + \left(\frac{dz}{dx}\right)^2\right]^{3/2}}{\frac{d^2z}{dx^2}} \tag{86}$$

$$r = \frac{x\left[1 + \left(\frac{dz}{dx}\right)^2\right]^{1/2}}{\frac{dz}{dx}} \tag{87}$$

x is the horizontal coordinate. Hence,

$$\frac{d^2z}{dx^2} + \frac{\frac{dz}{dx}}{x}\left[1 + \left(\frac{dz}{dx}\right)^2\right] = \left[\frac{2}{r_o} - \frac{g(\rho_L-\rho_V)z}{\sigma}\right]\left[1 + \left(\frac{dz}{dx}\right)^2\right]^{3/2} \tag{88}$$

Equation 88 can be reduced to dimensionless form by setting

$$X = x/r_o \tag{89}$$

$$Z = z/r_o \tag{90}$$

$$Z' = \frac{dZ}{dX} \tag{91}$$

$$Z'' = \frac{d^2Z}{dX^2} \tag{92}$$

Hence

$$Z'' + \frac{Z'}{X}\left[1 + (Z')^2\right] = \left[2-\hat{\beta}Z\right]\left[1 + (Z')^2\right]^{3/2} \tag{93}$$

$\hat{\beta}$ is defined by:

$$\hat{\beta} = \frac{g(\rho_L-\rho_V)r_o^{\,2}}{\sigma} \tag{94}$$

The ratio of the selected diameter to the equatorial diameter of the drop is defined as follows

$$S = d_s/d_e$$

In order to use equation 93 to evaluate the surface tension from pendant drop measurements, the function $\overline{H}$ is defined as follows:

$$\overline{H} = \hat{\beta}\left(\frac{d_e}{r_o}\right)^2 \tag{95}$$

For a given $\hat{\beta}$, the differential equation 93 can be solved numerically so as to determine d_e/ro and d_s/ro. Thus, S can be determined from:

$$S = \frac{d_s/r_o}{d_e/r_o} \tag{96}$$

$\overline{H}$ can be calculated from equation 95. By solving equation 93 for several values of $\hat{\beta}$ the relationship between S and $\overline{H}$ can be evaluated. The surface tension can be calculated from equation 94.

$$\sigma = \frac{g(\rho_L - \rho_V)d_e^{\,2}}{\hat{\beta}\left(\frac{d_e}{r_o}\right)^2} = \frac{g(\rho_L - \rho_V)d_e^{\,2}}{\overline{H}} \tag{97}$$

Equation 97 provides the basis for determining the surface tension from pendant drop measurements. Experimentally, the diameters, d_e and d_s, are determined. The shape factor S is then calculated and $\overline{H}$ determined. Equation 97 is then used to compute the surface tension.

Several authors (15,30,46) have solved equation 93 numerically and presented tabular results of $\overline{H}$ as a function of S. Stegemeier (47), using the results of Fordham (15) and Mills (30), found that when log $(1/\overline{H})$ is plotted against log S, a straight line results. From this he proposed the following equation for computing the surface tension from pendant drop measurements:

$$\sigma = (\rho_L - \rho_V) g (0.3127) \left(\frac{d_e}{d_s}\right)^{2.6444} (d_e)^2 \qquad (98)$$

σ is in dyne/cm., ρ is in gm/cm^3, d_e and d_s are in cm. Equation 98 provides a convenient method for computing surface tensions.

The pendant drop method was chosen for this study because of the many advantages of this method.

1. The contact angle does not enter into the results.
2. The method is not dynamic.
3. The measurements are made instantaneously.
4. Temperature control is simple.
5. The photographs serve as permanent record of the experiment.

Surface Tension Induced Motion In Drops

Surface tension induced motion in drops which are formed in another liquid have been reported by several authors (8,18,19,28,38). Most of these motions were noted in systems in which the drop was suspended in another immiscible liquid. If a component of low surface tension, which is soluble in both the liquid drop and the surrounding bulk liquid, is transferred from one phase to the other, motion can be induced. For example, when a toluene drop is suspended in water and acetone is squirted at the drop, a motion which has been described as a droplet kick is induced. Droplet oscillation has been noted by Ramshow and Thornton (38) in a drop suspended in air.

In the study of this report droplet kick was found in some of the systems investigated. The kick was particularly pronounced in systems which have components of largely different vapor pressures and differing surface tensions such as n-hexane and n-tridecane suspended in air.

Methods of Measuring Sonic Velocity

Reyburn (40) has measured the sonic velocity of several mixtures of n-hexane, cyclohexane, benzene, ethylbenzene, and n-tridecane using a pulse-type apparatus. The sonic velocity measuring equipment consisted primarily of a transmitter and a cylindrical sample cell containing the liquid to be studied. Transducers were situated at either end of the sample cell. At a specific instant a pulse was sent by the transmitter to the transmitting transducer and at the same time a pulse counter was activated. This ultrasonic pulse traveled through the liquid to the receiving transducer. Another pulse was then generated and sent to the transmitting transducer. The number of times the pulse traveled between the two transducers was registered as cycles/sec. The counter reading in cycles/sec. was converted into ultrasonic velocity in m/sec. by multiplying by the distance between the transmitters (m/cycle).

Reyburn concluded that Rao's correlation (39) can be used to calculate the sonic velocity of a mixture of the compounds he investigated with excellent results. The experimental data correlated with the sonic velocities predicted by Rao with an average error of about ±1%.

Other methods of measuring sonic velocities are described in the literature (4,16,35,41).

CHAPTER III

EQUIPMENT AND EXPERIMENTAL PROCEDURE

Surface Tension Apparatus

The apparatus used in this experiment was very similar to the one suggested by Andreas, et al. (2). A schematic diagram of this apparatus is shown in Figure 4.

The apparatus consists of a light source, a thermostatic bath with windows, a cuvette with a drop forming syringe and tip, and a single lens reflex camera, all of which are mounted on an optical bench.

The light source is a mercury arc lamp (Cenco type PG2190, 100 watts, high pressure) and a gelatin filter (Wratten No. 77-A) to provide monochromatic light. The lamp also contains a condensing lens, which is used to collimate the light beam. Monochromatic collimated light gives a more satisfactory image than ordinary light.

The temperature of the drop was controlled to 0.05°C by circulating water through the thermostatic bath from a constant temperature bath (Precision Science Model No. 66600). A refrigerated water circulation unit (Sargent S-84890) is also used to provide a heat sink for the temperature bath.

The inner chamber of the thermostatic bath was constructed to fit a glass cuvette (Curtin No. 4679A). A top was constructed for the cuvette from teflon to seal the drop from the atmosphere. The top was drilled to hold the drop forming syringe (Hamilton Microlite Syringe

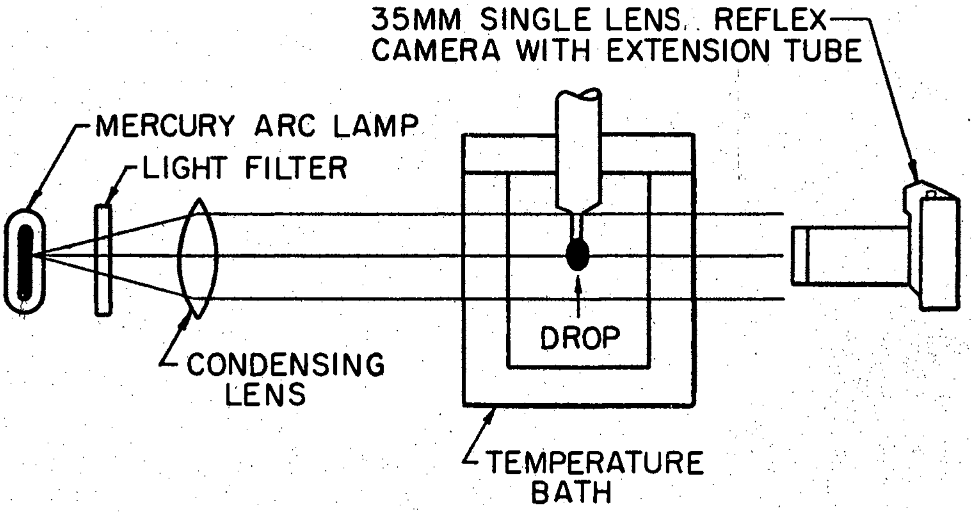

Figure 4. Pendant Drop Apparatus

No. 710) and a small thermometer used to help determine when the inner chamber had reached temperature equilibrium.

Drop forming tips were constructed from standard stainless steel hypodermic needles. Needles were constructed in two forms. For systems in which drops were suspended downward, the needles were cut off square to a length of about $1\frac{1}{2}$ inches. The tips were polished to eliminate irregularities in the shape of the needles. In this way the drop formed would be as symmetrical as possible. For systems in which a bubble is to be suspended pendant upward, the needle is first bent in a "fish hook" shape. The tip was cut square and polished. During polishing the tip of the needle was held firmly in the perpendicular position by means of a small brass block, which had a hole drilled the same size as the needle diameter. The tip was polished smooth with very fine emery cloth. A smooth perpendicular needle tip helps assure that the bubble formed will be symmetrical.

The camera was a standard 35-mm single lens reflex camera (Konica FS). In order to obtain close up photographs of the drop, a standard extension tube (Konica FP) was attached to the camera. Parts of two tubes were used to obtain a magnification of about one and one half.

The optical bench was contructed of two six foot pieces of three inch channel iron. The bench was fitted with four leveling screws. The weight of the bench and associated equipment was enough to eliminate vibrations. In addition, small rubber pads were placed under the feet of the bench to reduce high frequency vibrations. The light source was mounted on one end of the bench. Adjustment of the position of the lamp is possible by means of laboratory rack clamps. The

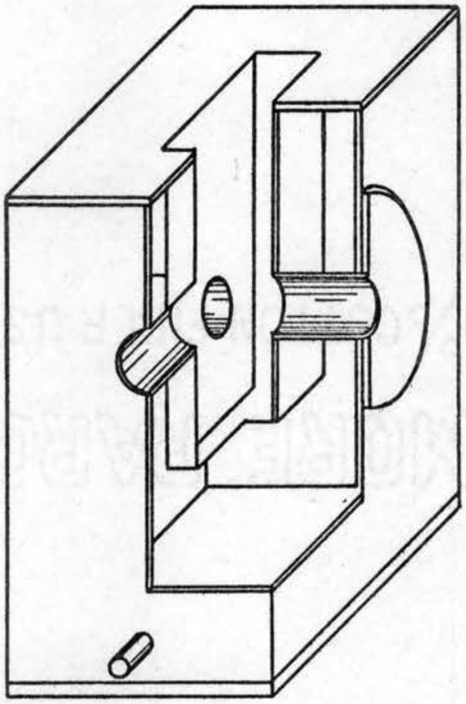

Figure 5. Thermostatic Bath

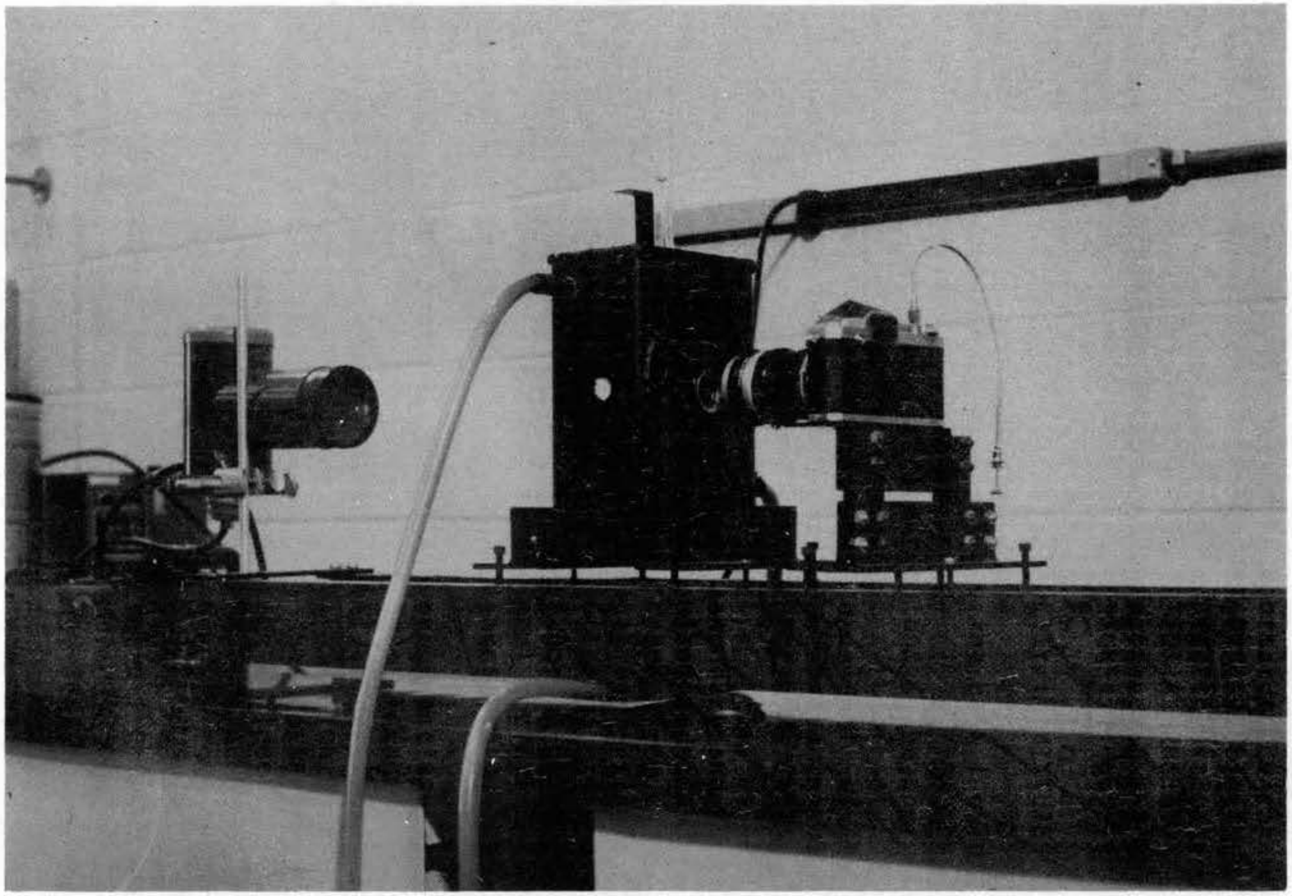

Plate I. Front View of the Pendant Drop Apparatus

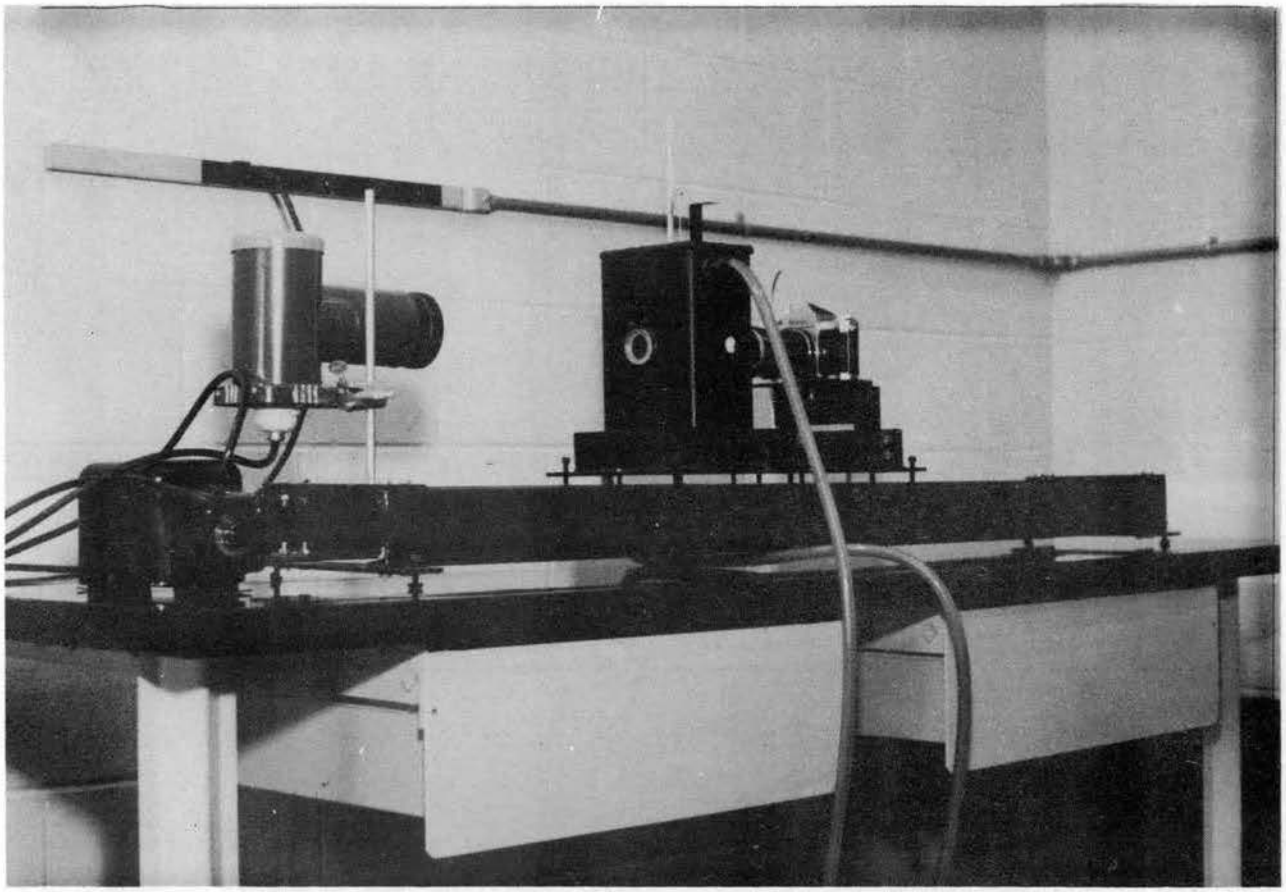

Plate II. Back View of the Pendant Drop Apparatus

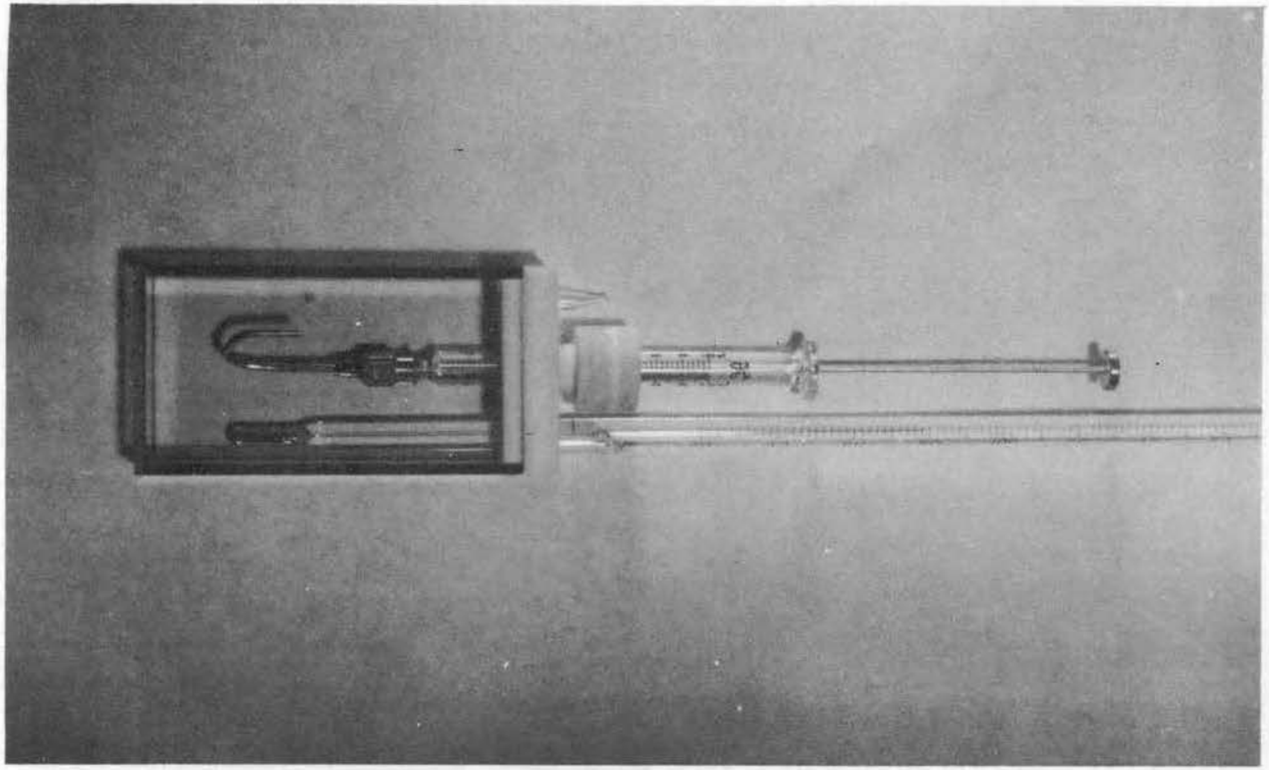

Plate III. Cuvette, Syringe, and Top

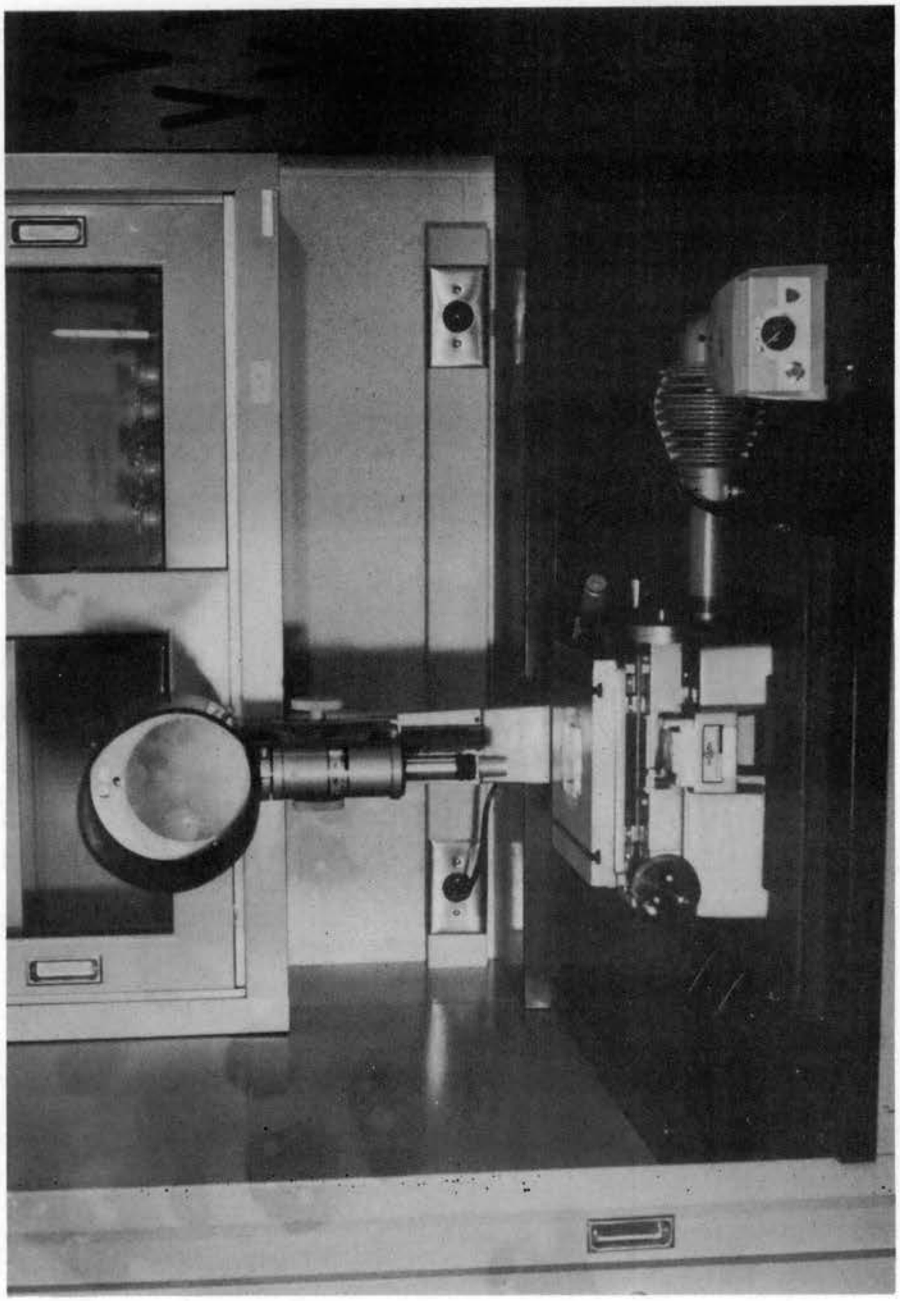

Plate IV. Toolmaker's Microscope

thermostatic bath also has four leveling screws to allow independent leveling of the bench and slight adjustments in the height of the bath. The bath is fastened to the bench by two clamps. A camera mount was also constructed. This mount can be leveled and clamped to the bench.

The temperature of the bath is measured with a Brooklyn thermometer (F3324 or C3227) which can be read to 0.01°C and which has been calibrated at the factory. Photographs taken with this apparatus are measured with a Gaertner Toolmaker's Microscope (M2001P).

Experimental Methods for Measuring Surface Tension

Surface tension measurements are made on the apparatus in the following manner. The bench, light source, thermostatic bath and camera mount are all leveled and adjusted so that a symmetrical bubble can be formed and photographed. The temperature bath is set and allowed to reach the desired temperature. The cuvette is partially filled with the liquid to be measured. The thermometer and syringe are fitted into the teflon top. The syringe is filled with air and the top is fitted into the cuvette. The cuvette is placed in the inner chamber of the thermostatic bath. The liquid in the cuvette is allowed to reach thermal equilibrium. A bubble of the largest size possible is formed. The photographs are taken, developed and measured. Finally the density of the liquid is measured with a pycnometer.

The apparatus must be leveled and adjusted so the needle will be perfectly vertical. The leveling process is accomplished by adjusting the various leveling screws until the needle when viewed through a telescope and compared with a plumb line is completely vertical. A small window in the side of the thermostatic bath is provided to aid in leveling. The position of the camera must be adjusted so that the image of the bubble is formed in the center portion of the camera lens. In this portion of the lense, aberration effects in the lens are minimized. The greatest accuracy is obtained by using only the center of the lens.

The temperature bath is set and the cooling and heating rate is adjusted so temperature control is within ±0.05°C.

The temperature within the cuvette usually reaches equilibrium within a period of thirty minutes to an hour. During this period, the small thermometer in the cuvette is observed until the temperature ceases to change.

The bubble must be formed very slowly to avoid dislodging it from the needle tip. The bubble size should be as large as possible so an accurate measurement can be made. Surface tension measurements can be made from any size bubble.

When photographing the bubble, the camera must be in perfect focus to avoid "fuzziness" around the edges of the drop on the photograph. Experience has shown the best way to focus the camera is to use natural room light reflected onto the bubble. The mercury arc lamp is too bright for the human eye to judge when the camera is in focus. The film used to make the photographs is Kodak High Contrast Copy film. This film is very slow (ASA No. 4) and requires a large amount of light for exposure. The film is extremely free of graininess and thus can be measured very accurately.

The film is obtained in one hundred foot rolls. The film is stored in a Daylight bulk film winder and lengths of film are cut from the roll as needed. After making the photographs, the film is developed in a Kodak Day-Load Tank using the following procedure. The film is soaked with each of four solutions and periodically agitated. The complete developing procedure is:

1. Bauman's Diafine Developer, solution A for 3 minutes.
2. Bauman's Diafine Developer, solution B for 3 minutes.
3. Rinse with tap water.
4. Kodak Rapid Fixer for 2 minutes.
5. Rinse with tap water again.
6. Kodak Photo Flo solution for $\frac{1}{2}$ minute.
7. Allow film to dry.

The negatives produced in this manner are measured directly with a Toolmaker's Microscope. Since the camera magnifies the image, the actual dimensions of the drop must be found by scaling the dimensions on the film from the measured dimensions of the dropper tip, d_n (Figure 3).

Density Measurements

The densities of the mixtures investigated in this study were measured by a pycnometer based on the design of Robertson (42). These pycnometers were Model TB-2250 Robertson Pycnometers (Scientific Glass Apparatus Co., Inc., Bloomfield, N. J.) graduated in 0.01 ml from 0 to 0.05 ml. They were calibrated with degassed, double distilled water at both 25°C and 45°C. These pycnometers had a whole range of graduations from which to read the volume, instead of the single hash-marks of many other pycnometers (see Figure 6).

The pycnometers were weighed dry and then weighed after being filled to some point on the graduations. With the weight of the liquid

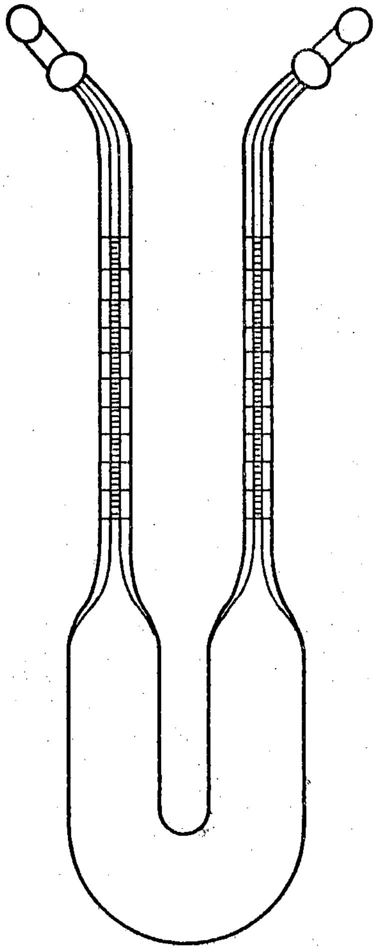

Figure 6. Modified Robertson Pycnometer

contained in each of the two pycnometers thus determined, they were placed in the constant temperature bath for thirty minutes. At the end of this time, the caps were removed briefly to allow the liquid levels in the two arms to equalize, and a scale reading was made. This scale reading gave the volume of the liquid in the pycnometer.

Sample Preparation

Five hydrocarbon liquids were chosen for study in this investigation. They were n-hexane, cyclohexane, benzene, ethylbenzene, and n-tridecane. All liquids are Phillips Petroleum pure grade (99 mole % minimum) chemicals and were used without further purification.

The samples of liquid mixtures were prepared by weight. An amount of one compound was placed in a glass stoppered weighing bottle and the weight of that component determined. Other components were added to the bottle in a similar manner and the weight of these additional components determined. During this mixing procedure care was taken to avoid, in as much as possible, evaporation losses from the bottle.

CHAPTER IV

RESULTS AND DISCUSSION

Experimental Results

Various mixtures of n-hexane, cyclohexane, benzene, ethylbenzene, and n-tridecane were made (66 binaries, 13 ternary, and 4 quaternary). The mixtures used in this experiment were chosen to compliment a viscosity investigation (40) currently underway. The compositions of these mixtures are presented in Appendix B.

The surface tension and density of each mixture was measured as described in the preceding chapters at 25° C and 45° C. These surface tension measurements are presented in Table III. In addition, the surface tensions for various binary mixtures are presented in Figures 7 through 9.

The sonic velocity for each mixture was determined from the pure component properties and the density of the mixture by assuming that the Wada (51) compressibility is linear with mole fraction. The results of these computations are presented in Appendix D.

From the plots of surface tension as a function of composition (Figures 7 through 9) the effect of Gibbs adsorption can be seen. For example in Figure 7 (benzene-n-hexane), the curve is concave upward. That is, the values of surface tension are lower than the mole fraction average surface tension. Molecules of lower surface tension components are adsorbed at the surface, lowering the surface tension.

TABLE III

EXPERIMENTAL SURFACE TENSIONS

	Surface Tension	
Mixture No.	25°C	45°C
n Hexane	17.90	15.86
Cyclohexane	24.27	21.58
Benzene	28.18	25.51
Ethyl Benzene	28.48	26.26
n-Tridecane	25.60	23.80
1	22.22	19.98
2	20.55	18.18
3	19.03	16.77
4	23.51	20.89
5	20.76	18.62
6	19.31	17.09
7	24.07	22.38
8	21.98	19.43
9	19.61	17.75
10	24.26	22.37
11	22.62	20.53
12	20.36	18.37
13	26.36	23.92
14	25.38	22.57
15	24.56	22.39
16	27.08	24.60
17	26.16	23.65
18	24.82	22.72
19	25.62	23.53
20	24.76	23.06
21	24.78	22.26
22	28.17	26.30
23	28.30	26.00
24	27.96	25.80
25	25.65	23.76
26	25.95	23.73
27	26.36	24.01
28	25.92	24.15
29	26.30	24.55
30	27.04	25.02
31	21.20	18.94
32	22.88	20.69
33	23.56	21.40
34	21.37	19.35
35	23.16	20.96
36	23.66	21.79
37	22.34	20.30
38	24.22	22.03
39	24.06	22.21

TABLE III (Continued)

Mixture No.	Surface Tension	
	25° C	45° C
40	25.39	23.44
41	26.16	24.15
42	27.60	23.94
43	26.79	24.12
44	22.32	20.39
45	23.54	21.89
46	24.31	22.30
47	24.34	22.25
100	22.99	21.09
101	21.25	19.05
102	19.69	17.83
103	19.41	17.54
104	18.53	16.27
105	19.44	17.20
106	20.74	18.86
107	23.15	20.98
108	26.25	23.66
109	20.46	18.58
110	23.20	21.21
111	25.98	23.85
112	19.42	17.45
113	21.96	19.85
114	24.66	22.81
115	25.04	22.85
116	26.10	23.36
117	26.84	23.92
118	25.08	22.46
119	26.45	24.06
120	28.09	25.71
121	24.56	
122	24.76	22.79
123	25.53	23.52
124	28.28	26.05
125	28.30	26.16
126	28.46	25.92
127	27.03	24.99
128	26.23	23.78
129	25.81	23.92
130	27.37	25.65
131	26.71	24.59
132	26.05	24.17

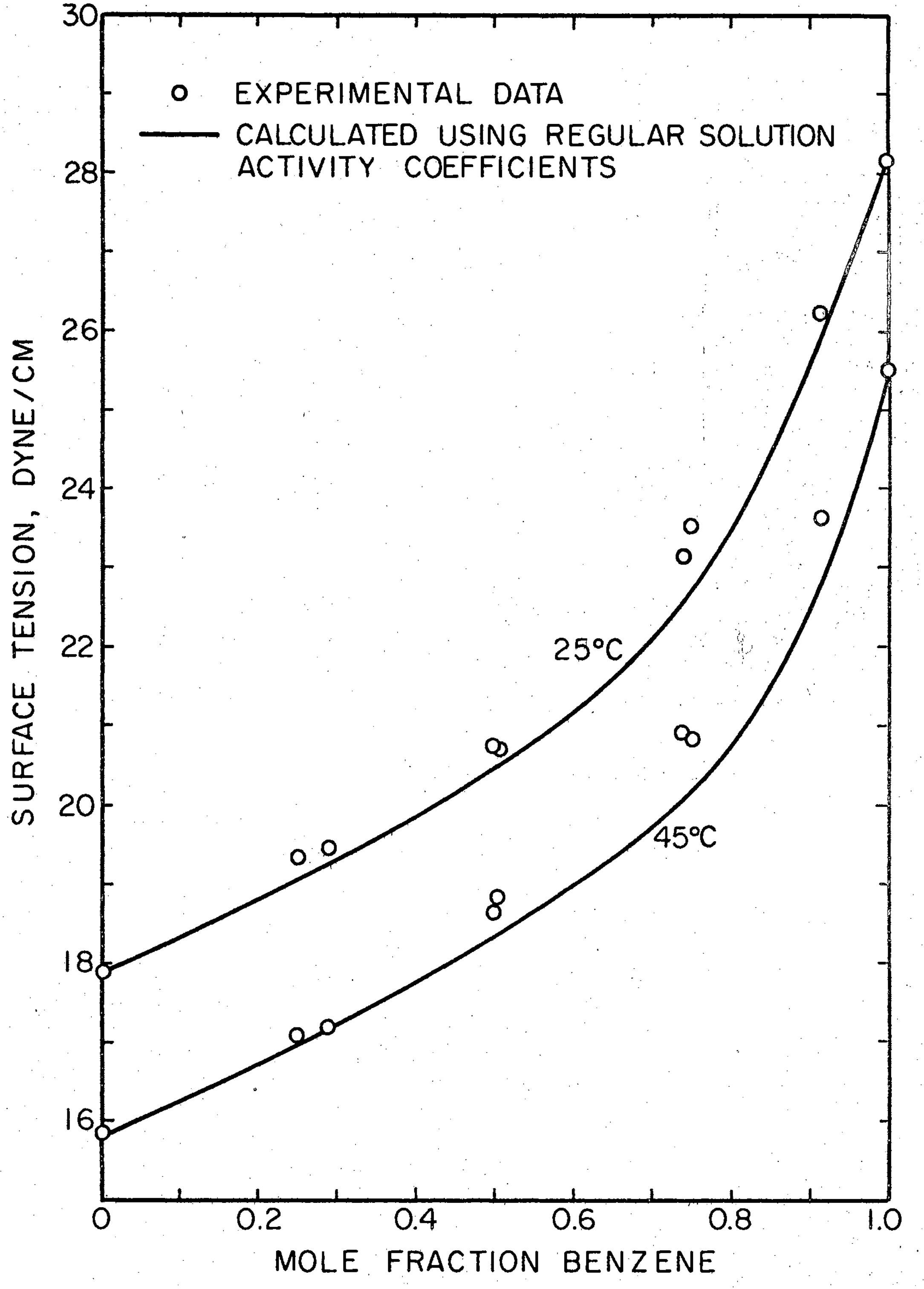

Figure 7. Effect of Composition on Surface Tension for the Benzene-N Hexane System. Experimental Data Compared with Calculated Surface Tension Values.

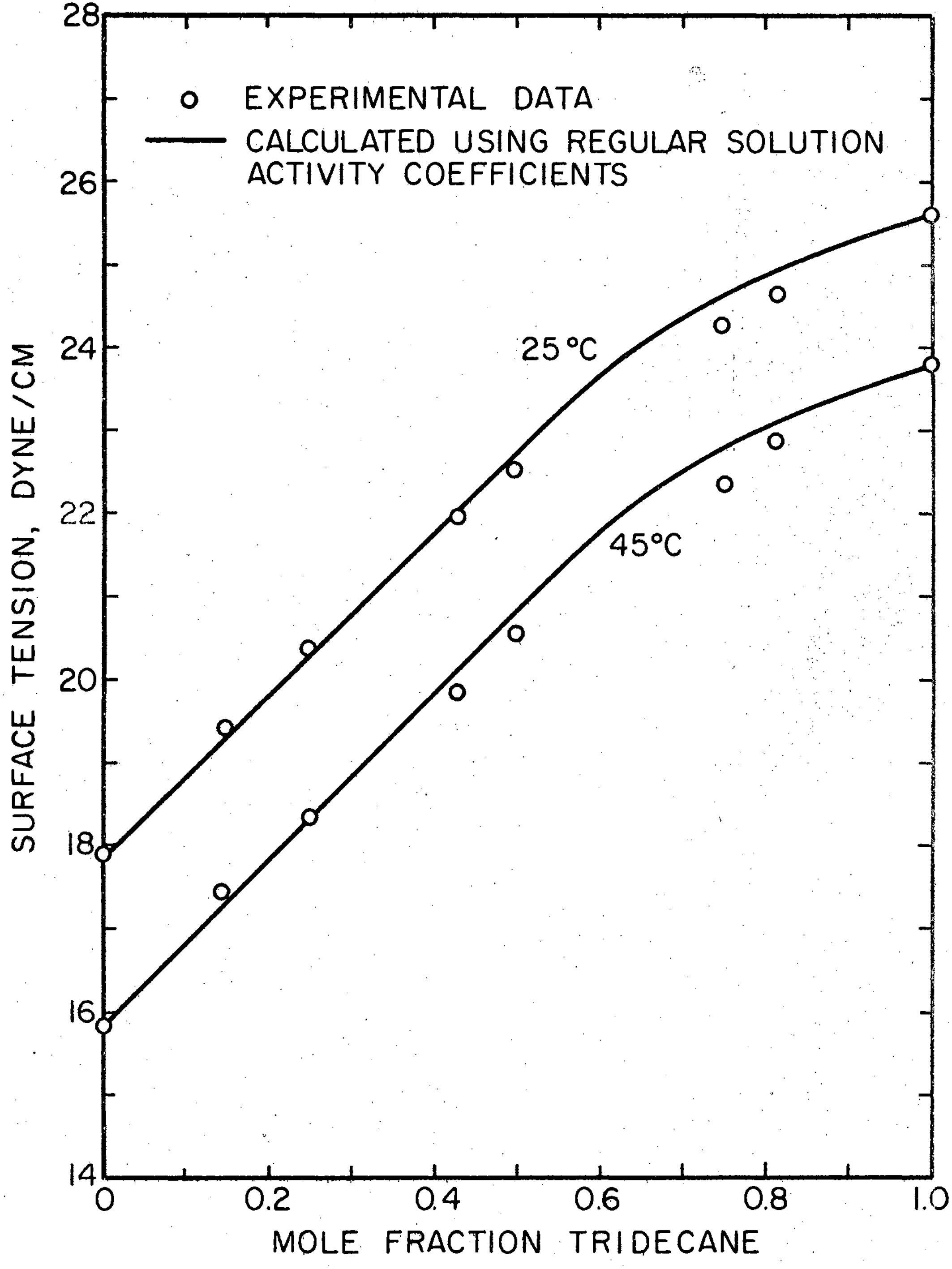

Figure 8. Effect of Composition on Surface Tension for the Tridecane-N Hexane System. Experimental Data Compared with Calculated Surface Tension Values.

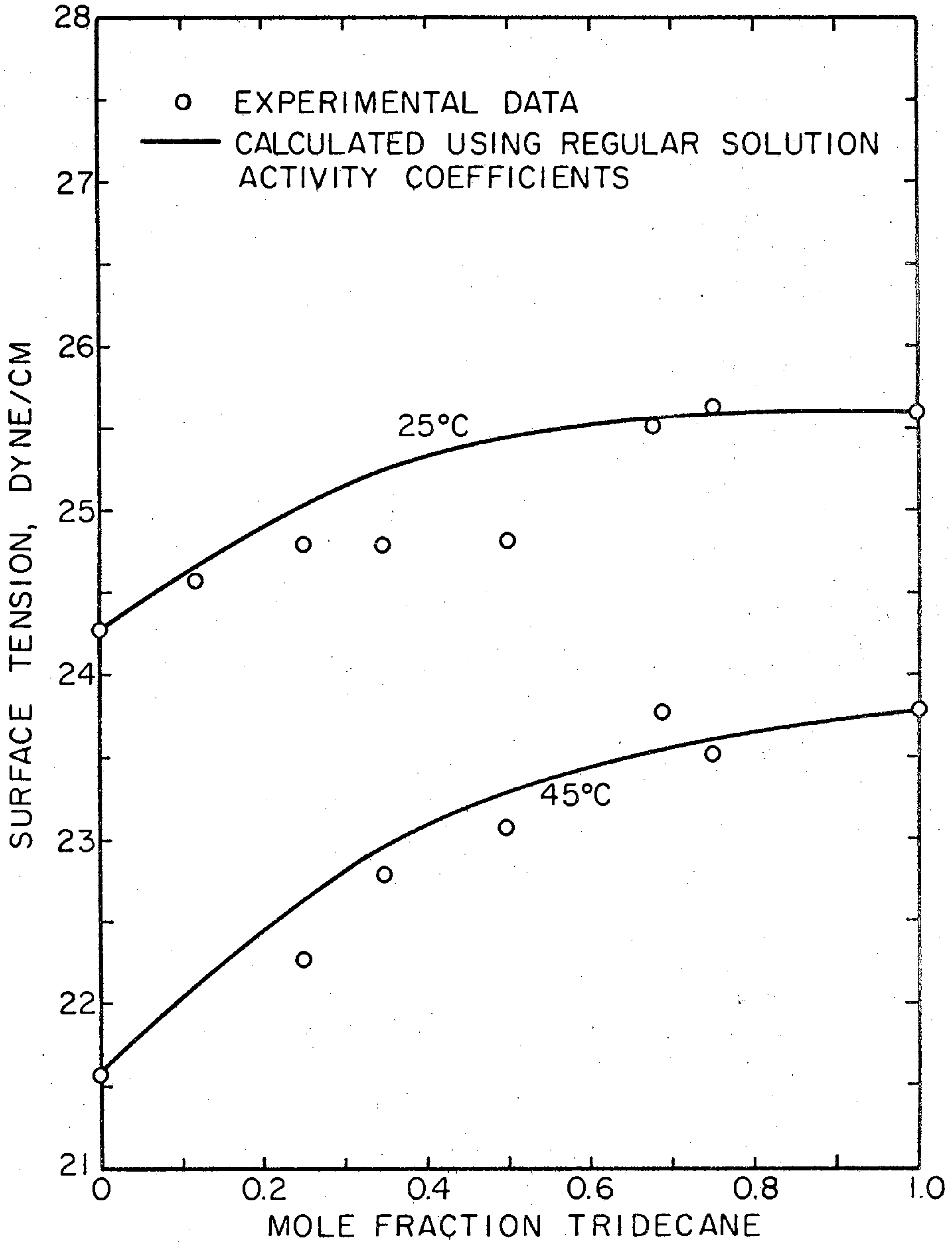

Figure 9. Effect of Composition on Surface Tension for the Tridecane-Cyclohexane System. Experimental Data Compared with Calculated Surface Tension Values.

The tridecane-n hexane and tridecane-cyclohexane curves (Figures 8 and 9) are exceptions to this type of plot. Here, the curves are concave downward. The effect is due to the larger size of the tridecane molecule as compared to either n-hexane or cyclohexane (compounds of lower surface tension). In mixtures, either of these smaller molecules are adsorbed at the surface to a larger extent than n tridecane. On the surface the n-tridecane molecules cover a much larger area fraction than the smaller molecules. Thus, a curve which is concave downward results. This effect can be accurately predicted by the method of Sprow and Prausnitz (44), shown in equations 58 through 67. The surface tensions for the binary mixtures of this study were calculated. The results are shown in Figures 7 through 9 and 15 through 21 as the solid lines. The experimental data are compared with the calculated results. The Sprow and Prausnitz (44) method reproduces experimental results with a fair amount of accuracy.

Evans and Clever (13) have reported a surface tension curve which is also not concave upward. These authors found that the surface tension of mixtures of isooctane and n dodecane were linear when plotted against mole fraction. They postulated that a special "molecular orientation" occured in the surface phase, causing a linear curve. Their data are shown in Figure 22 along with the calculated values. Again the method of Sprow and Prausnitz (44) is able to accurately predict the shape of the surface tension curves. Apparently, the presence of a special molecular orientation at the surface is not needed to explain experimental results.

Relationship Between Surface Tension and Sonic Velocity

In order to correlate surface tension and sonic velocity for mixtures, a relationship similar to equation 38 can be developed. The equation of state for a mixture is

$$P = \frac{RT}{V} - \left(\frac{\partial\Phi}{\partial V}\right)_T \tag{99}$$

Φ is the potential energy of the mixture. In order to apply equation 99, the potential energy of a mixture must be evaluated. As in developing equation 38, the assumption is made that the total potential energy of the liquid can be represented by equations which have a similar form to the intermolecular potential. If the non-nearest neighbor interactions are ignored, then the potential energy of a binary mixture is (37) approximately:

$$\Phi = X_1^2\Phi_{11} + 2\,X_1X_2\Phi_{12} + X_2^2\Phi_{22} \tag{100}$$

Φ_{ij} is the potential energy of the interaction between two molecules of species i and j. The intermolecular potential Φ_{11} and Φ_{22} are equal to the pure component interaction and can be expressed in form similar to equation 14.

$$\Phi_{ii} = \frac{\overline{B}}{V^b} - \frac{\overline{D}}{V^d} \tag{101}$$

The potential Φ_{12} usually cannot be evaluated directly. Φ_{12} is usually expressed in the form (20):

$$\Phi_{ij} = \frac{B'}{V^b} - \frac{D'}{V^d} \tag{102}$$

B′ and D′ are constants which are a function of temperature only. Usually B′ and D′ are expressed empirically in terms $\bar{B}$ and $\bar{D}$. Thus equations 100, 101, and 102 can be combined to yield:

$$\Phi = \frac{B}{V^b} - \frac{D}{V^d} \tag{103}$$

B and D are constants which are functions only of temperature and composition. By a procedure analogous to that used to develop equation 38, an expression can be derived to calculate sonic velocities of mixtures (35):

$$\frac{M\hat{U}^2}{\hat{\gamma}} = RT + b(b+1)BV^{-b} - d(d+1)DV^{-d} \tag{104}$$

M is the average molecular weight of the mixture and $\hat{\gamma}$ is the heat capacity ratio of the mixture. In order to use equation 104 the constants B and D must be evaluated in terms of physical properties of the mixture. Of course, from the equation of state (35) the following condition must hold:

$$PV = RT - DV^{-d} + BV^{-b} \tag{105}$$

Also in analogy with equation 38 (35):

$$\Phi_o = -DV^{-d} + BV^{-b} \tag{106}$$

Φ_o is the energy required to remove one mole of liquid with the same composition from the bulk liquid phase into the gas phase at constant temperature. Thus as with equation 38 the sonic velocity of a mixture is (35):

$$\frac{M\hat{U}^2}{\hat{Y}} = db\Phi_o + PV(d+b+1) - RT(d+b) \tag{107}$$

At this point Φ_o must be related to the surface tension of the mixture. Consider a process in which a small amount of liquid is evaporated from the bulk so the resulting vapor is in equilibrium with the liquid. Then the energy required to perform this evaporation is in analogy with equation 38.

$$\Phi^* = 2(K_1X_1\Omega_1 + K_2X_2\Omega_2)\left[\sigma - T\left(\frac{\partial\sigma}{\partial T}\right)_A\right] \tag{108}$$

Φ^* is the energy required to evaporate a small amount of liquid at equilibrium, and K_1 is the vapor-liquid equilibrium constant of species 1. Φ^* can be related to Φ_o by

$$\Phi_o - \Phi^* = (H_v{}^o - H) - (H_v{}^* - H) \tag{109}$$

H_v^o is the enthalpy of a vapor which has a composition equal to the composition of the bulk liquid, H_v^* is the enthalpy of the vapor with a composition which is in equilibrium with the bulk liquid, and H is the enthalpy of the liquid. Combining equations 108 and 109 yields:

$$\Phi_o = 2(K_1X_1\Omega_1+K_2X_2\Omega_2)\left[\sigma-T\left(\frac{\partial\sigma}{\partial T}\right)_A\right]+(H_v^o-H_v^*) \tag{110}$$

A complete derivation of equation 110 is presented in the appendix. Equation 110 provides a relationship between Φ_o and surface tension for a mixture. Unless the K value and enthalpy relationship are known this equation cannot be used. On the other hand, a good approximation of this equation can be made by assuming that the surface area of each species is not greatly different from the other. Therefore;

$$(K_1X_1\Omega_1+K_2X_2\Omega_2) = V^{2/3}N^{1/3} \tag{111}$$

V is the molar volume of the mixture. Also, if the vapor enthalpy of each component is approximately equal, then $H_v^o-H_v^*$ can be neglected.

$$\Phi_o = 2V^{2/3}N^{1/3}\left[\sigma-T\left(\frac{\partial\sigma}{\partial T}\right)_A\right] \tag{112}$$

Equations 107 and 112 can be used to estimate the sonic velocity of a mixture. Normally the dependence of the surface tension on temperature is not known for the mixture, thus these two equations cannot be conveniently used. An approximation suggested by Nozdrev (35) can be applied.

$$\Phi_o = C\sigma V^{2/3}N^{1/3} \tag{113}$$

C is an arbitrary constant which applies to all liquids. The value of the constant C can be determined from experimental data. Hence, the relationship between sonic velocity and surface tension can be found by combining equations 113 and 107.

$$\frac{M\hat{U}^2}{\hat{\gamma}} = (CdbN^{1/3})\sigma V^{2/3} + PV(d+b+1) - RT(d+b) \qquad (114)$$

The surface tensions, densities, and calculated sonic velocities of this study were used to evaluate the constant in equation 114. The constants d and b were found to have only small effects on the final results. Possibly if a larger temperature range had been used in this study a greater effect would have been observed. Thus, the values of b and d were chosen to be 2 and 4. These values correspond to the exponents in the Lennard-Jones 6-12 intermolecular potential model. The value of the heat capacity ratio was assumed to equal 1.4 for all mixtures. Based on these assumptions the value of C was determined to be:

$$C = 2.94 \qquad (115)$$

Figure 10 shows the experimental surface tensions plotted as a function of the surface tension obtained from equation 114. As can be seen the values fall very close to the diagonal. The data fits equation 114 with an average absolute per cent error of about 4%. Because of the arbitrary nature of the constant C, its value of 2.94 is expected to apply only to hydrocarbons of the type used in this study.

The slope of the data points shown in Figure 10 appear to be somewhat different from the diagonal. In deriving equation 110 several assumptions and approximations were made. The deviation of the points from the diagonal is probably a result of these simplifications.

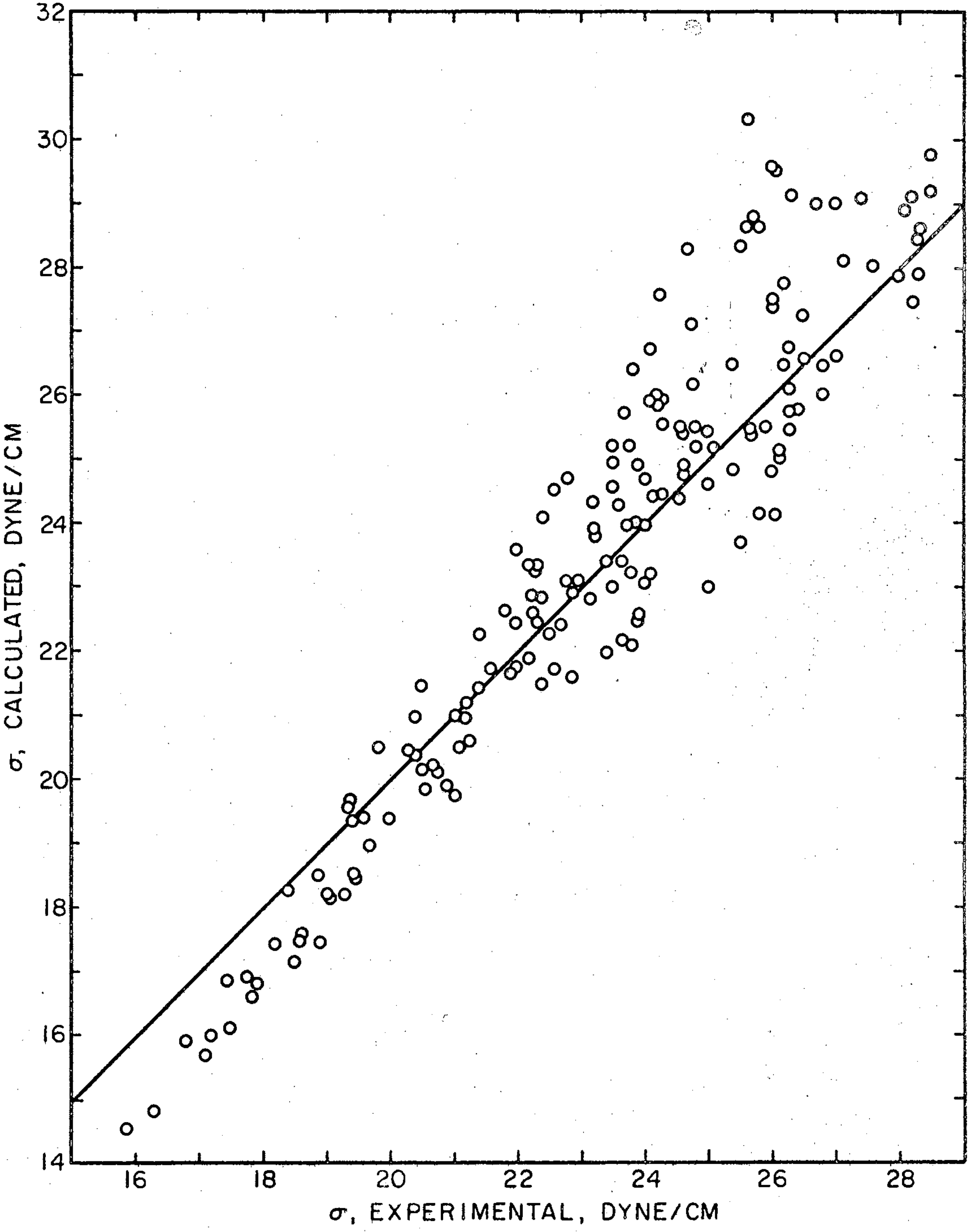

Figure 10. Comparison of Equation 114 with Experimental Data

Comparisons of equation 38 with equations 107 and 112 show that the equation for pure components also apply approximately to mixtures. Therefore, other correlations of sonic velocity and surface tension for pure components are also expected to apply for mixtures.

An attempt was made to correlate the data of this study in accordance with the Auerbach (3) equation. Surface tension, σ, was plotted against the density times the sonic velocity raised to the three halves power, $\hat{U}^{3/2}$. The resulting line was straight. The intercept did not pass through the origin as was expected from equation 6. Also the slope of the line was not 6.3 X 10^{-4}, as was found by Auerbach, but was some number slightly smaller. Auerbach's equation was altered slightly by the addition of a constant to allow the equation to have some intercept other than zero. By the method of least squares, an expression was determined which fits the experimental data.

$$\sigma = 3.9166 + 6.053 \times 10^{-4} \rho \hat{U}^{3/2} \tag{116}$$

A plot of experimental surface tension against surface tensions calculated from equation 116 is shown in Figure 11. The average value of the absolute per cent error in this correlation is about 2%. This equation gives results which are better than equation 114.

Surface Tension of Mixtures

The data of this experiment were compared with the method developed by Weinaug and Katz (52) shown in equation 75. The equation assumes that the parachor of a mixture is equal to the summation of pure component parachor times their mole fraction in the mixture.

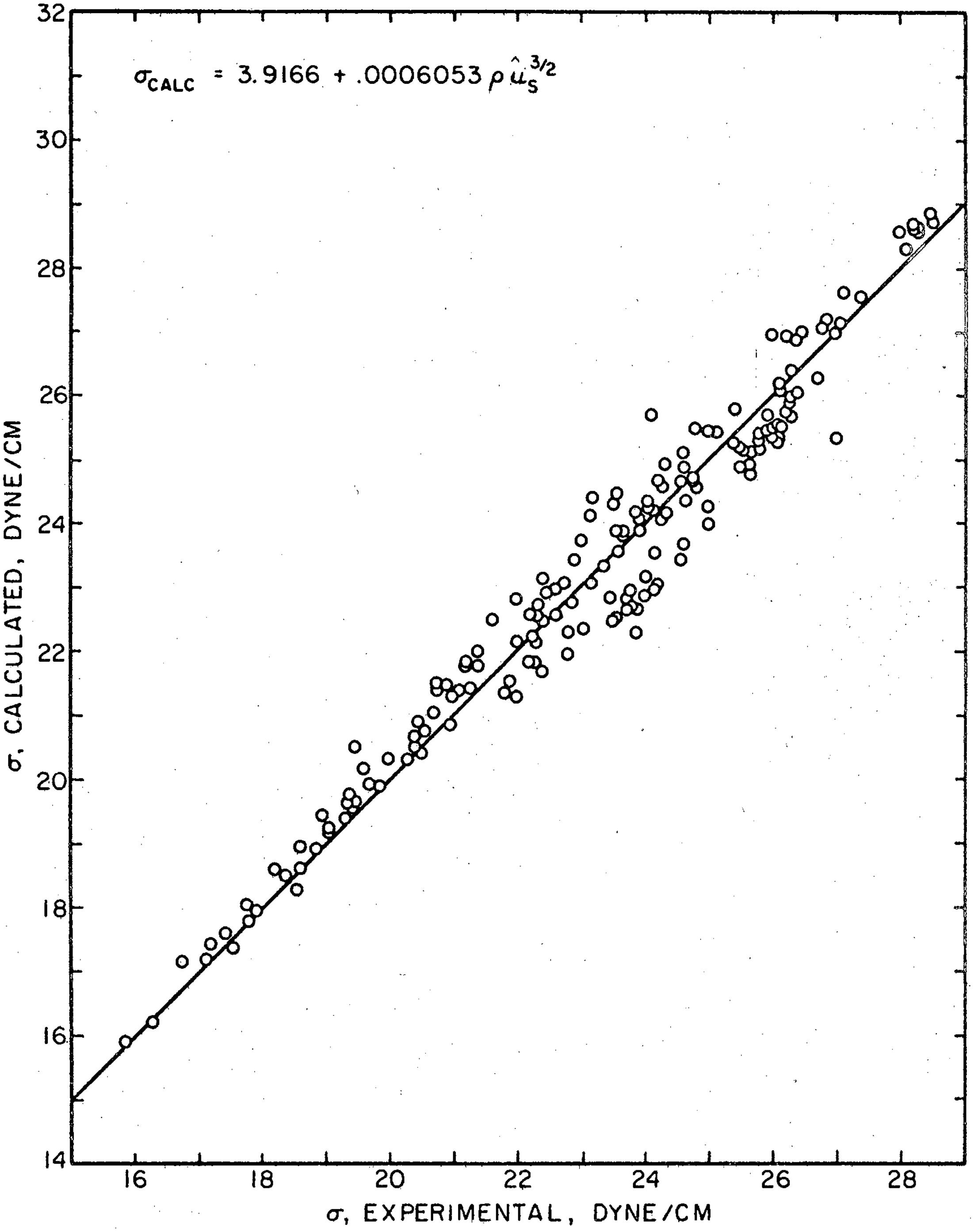

Figure 11. Comparison of Equation 116 with Experimental Data

The results of this comparison are shown in Figure 12. The average difference between the calculated and the experimental values for this method is about ±3%. The method provides an adequate procedure for estimating the surface tension of a mixture of hydrocarbons. Data of this experiment can be fitted better by equation 116.

Experimental Errors

The experimental error in the surface tension measurements is estimated to be less than ±1%. Andreas, Hauser, and Tucker (2) have suggested, on the basis of experience, that if a probable error of not more than ±0.1% in the linear measurements is made, then the resulting error in the surface tension is about ±0.5%. The optical comparator used in this experiment can be read accurately to ±2 microns. This error usually means about ±.12% error in the linear measurement. If the observations by Andreas et. al. are correct then an error of 0.6% is to be expected.

A comparison of the surface tensions of the pure components measured in this investigation with the surface tensions published in the literature was made. The comparison is presented in Table IV. The results show that the average per cent error is less than ±0.6% as expected from the rule of Andreas et al.

Of course, the simple rule presented by Andreas et al. cannot describe the actual error propagation in the surface tension measurement. Stauffer (46) has presented an analysis of the error propagation in the pendant drop technique. One reason the per cent error in the surface tension is so much larger than the per cent error in the linear measurements is that the measured equatorial diameter is used to locate

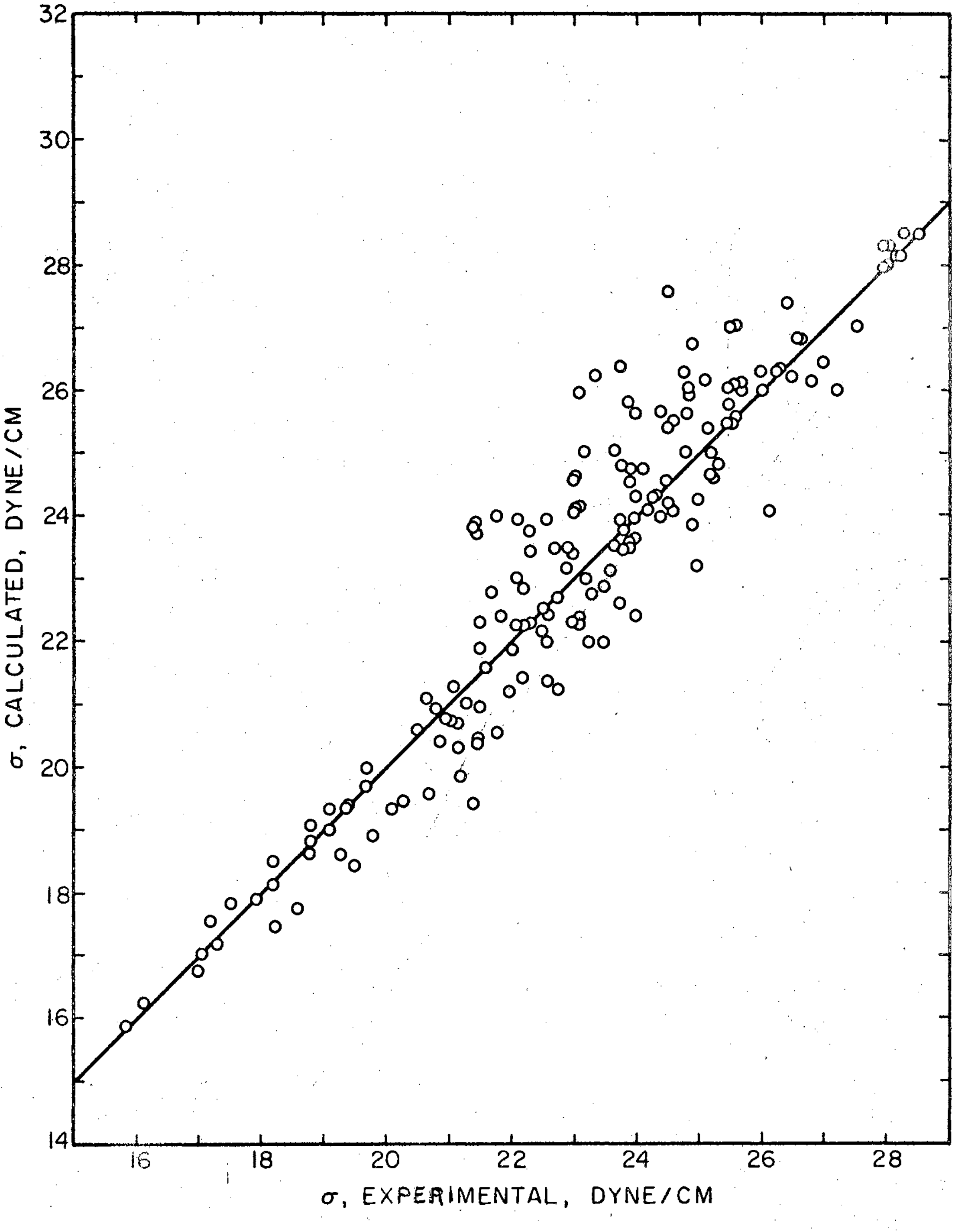

Figure 12. Comparison of Weinaug and Katz (52) Equation with Experimental Data

TABLE IV

PURE COMPONENT SURFACE TENSIONS

Component	Temperature, °C	Surface Tension, dyne/cm.		% Error
		Literature*	Experimental	
n-Hexane	25	17.90	17.82	0.45
	45	15.86	15.98	0.76
Cyclohexane	25	24.27	24.36	0.37
	45	-----	21.58	----
Benzene	25	28.18	28.28	0.35
	45	25.51	25.32	0.75
Ethyl Benzene	25	28.48	28.62	0.49
	45	26.26	26.12	0.55
n-Tridecane	25	25.60	25.50	0.39
	45	23.85	23.97	0.50

*All literature values were taken from API Report No. 44 except cyclohexane which was taken from (13) at 25°C.

the selected plane from which the selected diameter is measured. If an error is made in the measurement of the equatorial diameter, d_e, the incorrect plane is selected for measurement of the selected diameter, d_s. Thus, an erroneous measurement of d_s will be made. In addition, this measurement is also subject to normal experimental error of linear measurement. This means that the experimental error is a function of the shape of the drop. Stauffer accounted for this effect and determined the probable errors as a function of the shape factor, S. A detailed analysis of the error of propagation in the measured surface tension by the pendant drop method is presented in the appendix. The results of this analysis are presented in Figure 13 for a 1% error in the comparator reading. Figure 13 points out the necessity for photographing the largest possible drop. As can be seen when S is large, corresponding to a large drop size, the error is small. Thus the larger the drop the smaller the error.

The results of a typical run are presented in Table V. The 95% confidence interval for the data was determined by standard statistical procedures. The resulting probable error was thus determined to be ±0.596%. For a ±0.12% error in the linear measurement or ±0.06% error in the comparator reading, the probable per cent error from the propagation of error analysis of Figure 13 is ±0.699%. Therefore, the variations in the measured surface tension are mostly determined by the precision with which the linear dimensions can be measured. If improvements are to be made in the experimental procedure, then this is the area which deserves the most attention.

There are several other factors which can affect the results of the surface tension measurements. An important consideration is the

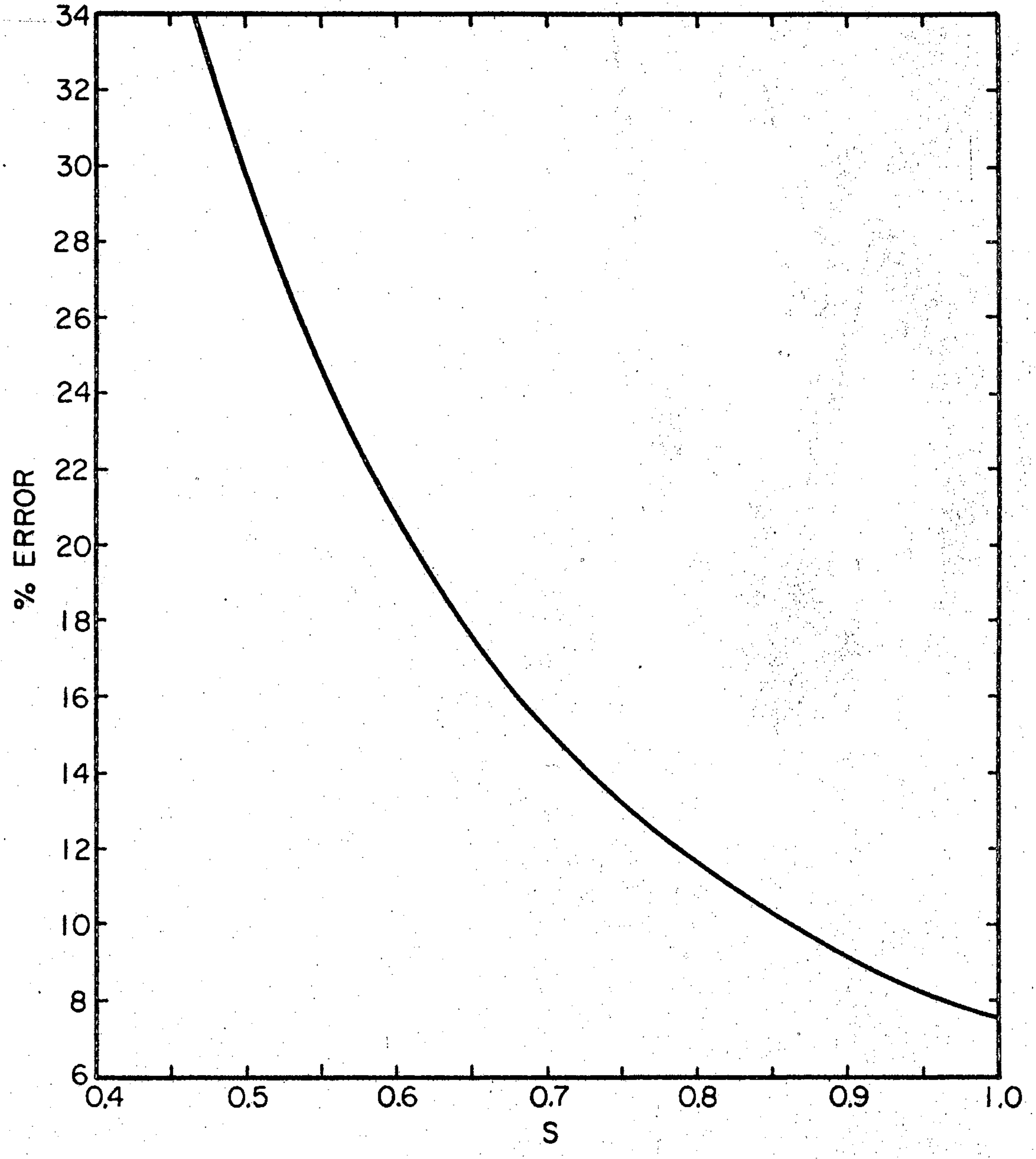

Figure 13. Probable Limits of Error in Surface Tension with an Experimental Error in Comparator Reading of 1%

TABLE V

ANALYSIS OF ERROR IN A TYPICAL RUN

Measurement No.	Calculated Surface Tension (dyne/cm)
1	23.31
2	23.40
3	23.52
4	23.57
5	23.56
$S = d_s/d_e$	0.797
Average Surface Tension	23.47
Standard Deviation	0.1131
Lower Limit on 95% Confidence Interval	23.33
Upper Limit on 95% Confidence Interval	23.62
Probable Limits of Error In Surface Tension at 95% Confidence Level	±0.596%

distortion in the camera lense. Experience has shown that the image formed is slightly distorted because of very slight imperfections in the lens of the camera. This distortion is pronounced near the edges of the frame. In the region of the center of the frame the distortion is very slight. For this reason, all photographs were taken near the center of the field of view in the camera. One important factor to remember is that measurements of the needle diameter, d_n, which is used to determine the magnification factor, should be made as near the tip of the needle as possible. In this way the measurement will be made as near the drop as possible, thus the determined magnification factor will represent the magnification of the photographed drop.

All vibrations must be eliminated from the apparatus because of several reasons. Vibrations create dynamic effects and then disrupt the equilibrium at the surface. Also, vibrations cause distortion in the shape of the drop. In addition, the motion of the drops creates a large amount of fuzziness at the edge of the photograph of the image.

The equipment must be properly leveled. If not, then the drop formed will not be symmetrical. Thus, the assumption that the drop formed is a surface of revolution, made in the solution in the differential equations of the drop shape equation, will no longer be valid. In this respect, the needles must be manufactured with care. The needles must have a clean cut on the end.

Finally, the pure components used in the experiment must be free of surface active materials. These materials exhibit their presence by a reduction of the surface tension with age. No significant effect of time on the surface tension was noticed in this experiment.

Using the results presented in Table IX, the error in the calculated sonic velocities is expected to be less than about ±1%. Density measurements are accurate to ±0.0005 gm/cc. Thus the per cent error in the density is very small.

If the per cent error in the surface tension is about ±1% and the sonic velocity error is about ±1%, then an average per cent error of ±2% in the correlation of sonic velocity is not unreasonable.

Surface Tension Induced Motion

The surface tension of pure components can be adequately measured with the apparatus of this work, when drops of liquid are photographed as suggested by Andreas et al. (2). When mixtures containing components of significantly different physical properties are to be measured, drops cannot be used. This is because of the difficulties involved in trying to completely eliminate evaporation from the drop. While most evaporation can be eliminated by a close fitting top for the cuvette, there still exists a very slight evaporation caused by minute leaks of vapor through the top. This evaporation is not large enough to significantly change the volume or the bulk composition of the drop over the short period of time required to make the photographs. The evaporation is large enough to induce composition and surface tension gradients in the drop, if the drop contains components of differing volatility and surface tension. The surface tension gradients while small are still large enough to create a force which can induce motion in the drop. This motion creates dynamic effects which can disturb the equilibrium at the interface. In addition, the motion becomes strong enough to distort the shape of the drop, thus giving an erroneous measurement of the surface tension.

Several photographs of droplets in which motion has been induced by evaporation are shown in Plate V. By observing the droplets and studying motion pictures of these drops, the motion was found to be induced in the following manner. During the initial formation of the drop, part of the liquid climbs the wall of the needle because of the wettability of the hydrocarbons used in this study. This thin film evaporated slightly, increasing the surface tension of this part of the liquid. As more of the drop is formed, this brings into contact with the film a drop which has a lower surface tension. Thus, the gradient induced across the film causes the film to move further up the needle and forms a smaller droplet higher up on the needle. As more of the drop is formed, more liquid tends to move up the needle. This process continues until the weight of the liquid on the upper portion of the needle overcomes the surface tension forces. Then a small droplet of liquid descends from the upper part of the needle and comes in contact with the fully formed drop. Because the descending droplet has a higher surface tension than the bulk, a strong gradient is formed at the point where the lower drop clings to the needle. This causes the main drop and the smaller droplet to move upward very quickly. Of course, the film on the needle is then renewed and the evaporation of the new film begins and the entire process is repeated.

The effect of the slight evaporation can be avoided by using air bubbles suspended from the tip of a "fish hook" shaped needle in the cuvette partially filled with the liquid to be measured. Since the volume of the bubble is relatively small, the air in the bubble is

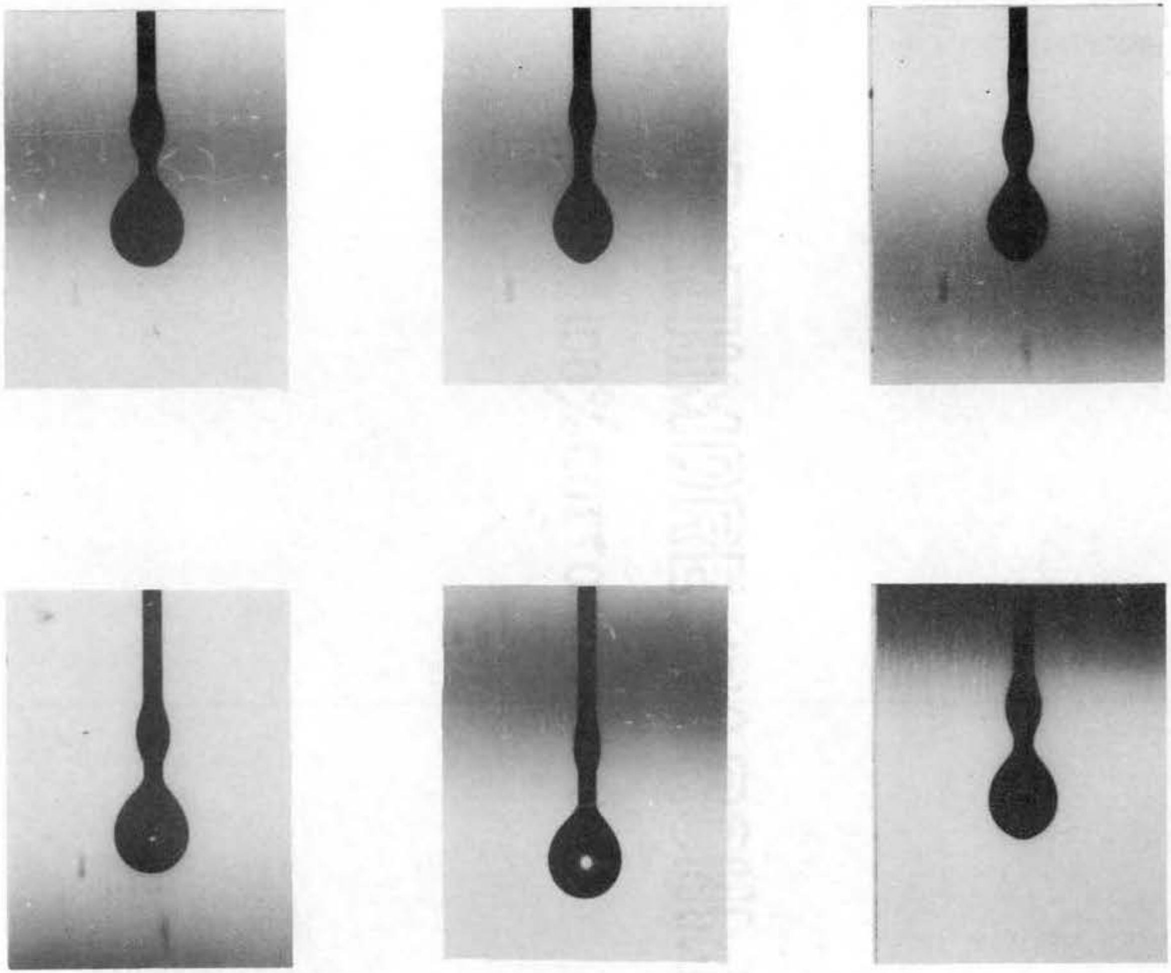

Plate V. Oscillating Droplets

quickly saturated with vapor, preventing further evaporation from the surface of the bubble. Consequently, motion of the surface is eliminated. In addition the larger amount of liquid present reduces the possibility of concentration gradients forming in the region of the surface.

Of course, the bubble will be suspended pendant upward. Measurements and calculations are made on the bubble in exactly the same manner as they are on the drops.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

The empirical correlation of surface tension and sonic velocity based on Auerbach's (3) equation, provides a very good method of estimating the surface tension of hydrocarbons and their mixtures. This correlation fits the data of this study with an average error of about ±2%. This relationship is expected to apply only at temperatures near room temperature. Certainly it is expected to apply only at temperatures well below the critical point.

Future research in the field of surface tension of mixtures should be carried out. Of particular interest are mixtures of long chain hydrocarbons with hydrocarbons whose molecules have a small surface area. The orientation effects of the molecules in these types of mixtures should provide very useful information which will aid in the development of a more general method for predicting the effect of composition on surface tension for hydrocarbons. In order to obtain useful results, at least the following properties of the pure components must either be taken or known from the literatures: (1) surface tension, (2) ideal and saturated enthalpies of the vapor phase, (3) vapor pressure, (4) density, (5) dependence of surface tension on temperature, and (6) vapor-liquid equilibrium data, which can be used to determine the bulk phase activity coefficient. With this information equations

63 through 68 can be used to accurately estimate the surface tension of mixtures.

The Sprow and Prausnitz (45) and the Katz and Weinaug (5) methods provide accurate means of estimating the surface tension of mixtures. Both of these methods fit the data of this study.

The Auerbach equation is a very useful method of correlating surface tension and sonic velocity. A detailed study of the effect of temperature on the constants of this equation has not as yet been carried out. The numerical values of these constants do not appear to vary over a large range. Of course, no studies as yet have been carried out on the effects of pressure on these constants. These effects should be studied. For the purposes of this investigation, the surface tension, sonic velocity, and density of pure components can be measured at various pressures and at temperatures from near the freezing point to near the boiling point. Conditions near the critical point should be considered.

Refinements in the apparatus used in this experiment can be made. In order to obtain greater precision in the surface tensions measurements, a camera which yields images with a larger magnification would be very useful. If a magnification of about 10 times greater than that obtained with the camera used in this experiment is used, then surface tension measurement could be made with a precision of 0.1%. In order to obtain high quality images, the optical system of the camera would have to be greatly improved to eliminate unwanted aberrations.

Further improvement can be made in the apparatus by changing the leveling mounts on the base of the thermostatic bath and the camera. At present leveling of the apparatus is a very tedious job. Improved mounts would allow a more accurate positioning of the drop and camera and would insure that a completely symmetrical drop could be formed.

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NOMENCLATURE

A	Surface Area
a_i	Activity of component i
a_i^s	Activity of component i in the surface phase
B	Constant
B_1	Constant
$\bar{B}$	Constant
B'	Constant
b	Constant
b_1	Constant
C	Constant
C'	Constant
D	Constant
D_1	Constant
$\bar{D}$	Constant
D'	Constant
d	Constant
d_1	Constant
d_e	Drop equatorial diameter
d_n	Drop forming needle diameter
d_s	Drop selected plane diameter
F	Helmholtz free energy
f	Molecular shape factor
g	Local acceleration of gravity

H	Enthalpy of the liquid
$\overline{H}$	Drop shape factor
H_v^o	Enthalpy of a vapor which has a composition equal to the bulk liquid composition
H_v^*	Enthalpy of the vapor which has a composition that is in equilibrium with the bulk liquid
h	Planck's constant
h_i^{id}	Enthalpy of species i in the ideal state
h_i^{sat}	Enthalpy of species i at saturation
Δh_i^{vap}	Heat of vaporization of species i
j	Any physical property
K_i	Vapor-Liquid equilibrium constant
$\hat{K}_i$	Distribution coefficient of component i
k	Boltzman's constant
L	Intermolecular free length
L_{Hex}	Intermolecular free length for a hexagonal packing
l	Length
ℓ	Intermolecular distance
M	Molecular weight
M_L	Molecular weight of the liquid phase
M_V	Molecular weight of the vapor phase
m	Mass per molecule
N	Avogadro's number
P	Pressure
$\hat{P}_i$	Parachor of species i
P_i^{sat}	Vapor pressure of species i
R	Gas constant
$\overline{R}_A$	Rao's molecular sonic velocity

r and r'	Principal radii of curvature on the surface of a drop
r_o	Radius of curvature at the origin of the drop
S	Ratio of the drop selected diameter to the equatorial diameter
$\hat{S}$	Separation factor
s	Entropy
T	Temperature
T_c	Critical temperature
$\hat{U}$	Sonic velocity
$\hat{U}_{20}$	Sonic velocity at 20°C
u	Internal energy
V	Volume per mole
v	Volume per molecule
V_o	Molecular volume at absolute zero
V_T	Molecular volume at T temperature
W_i	Weight fraction of component i
$\overline{W}$	Wada's molecular compressibility
X	Dimensionless horizontal drop coordinate
X_i	Mole fraction of component i in the liquid phase
x	Horizontal drop coordinate
Y_i	Mole fraction of component i in the vapor phase
$\hat{Y}$	Total surface area of a molecule
Z	Dimensionless vertical drop coordinate
z	Vertical drop coordinate

Greek Letters

$\hat{\beta}$	Drop shape parameter
β_s	Adiabatic compressibility

γ_i	Activity coefficient of component i
$\hat{\gamma}$	Heat capacity ratio
γ_i^S	Activity coefficient of component i in the surface phase
δ_i^s	Square root of the surface cohesive energy density
$\bar{\delta}^s$	Surface area average square root of the surface coheseive energy density
δ_{Rev}	Reversible heat
δ_w	Work done by the system
ϵ	Error in comparator reading
θ_i	Surface area fraction of component i
λ	Heat of vaporization
μ_i	Chemical potential of component i
μ_i^M	Chemical potential of component i in a mixture
μ_i^s	Chemical potential of component i in the surface phase
μ_i^{MS}	Chemical potential of a component i in a mixture surface phase
σ	Surface tension
σ_{20}	Surface tension at 20°C
σ^M	Surface tension of a mixture
σ_{X1}	Error in the calculated surface tension as a result of an error in measuring x_1
ρ	Density
ρ_L	Density of the liquid phase
ρ_V	Density of the vapor phase
Φ	Potential energy
$\Phi^{(\ell)}$	Potential energy as a function of the intermolecular distance
Φ_o	Energy required to move one mole of liquid from the liquid phase to the gas phase under equilibrium conditions
Φ^*	Energy required to vaporize a small amount of liquid from a mixture at equilibrium

Ω	Surface area per mole
$\bar{\Omega}$	Partial molar surface area of species i.
ω	Surface area of one molecule

APPENDIX A

COMPOSITIONS OF MIXTURES

TABLE VI

COMPOSITIONS OF MIXTURES

Mixture	Mole Fraction				
No.	n-Hexane	Cyclohexane	Benzene	Ethyl Benzene	n-Tridecane
1	.2502	.7498			
2	.5008	.4992			
3	.75	.25			
4	.25		.75		
5	.50		.5		
6	.75		.25		
7	.25			.75	
8	.5			.5	
9	.75			.25	
10	.25				.75
11	.5				.5
12	.75				.75
13		.25	.75		
14		.5	.5		
15		.75	.25		
16		.25		.75	
17		.5		.5	
18		.75		.25	
19		.25			.75
20		.5			.5
21		.75			.25
22			.25	.75	
23			.5	.5	
24			.75	.25	
25			.25		.75
26			.5		.5
27			.75		.25
28				.25	.75
29				.5	.5
30				.75	.25
31	.5	.25		.25	
32	.25	.5		.25	
33	.25	.25		.5	
34	.5	.25			.25
35	.25	.5			.25
36	.25	.25			.5
37	.5			.25	.25
38	.25			.5	.25

TABLE VI (Continued)

Mixture	Mole Fraction				
No.	n-Hexane	Cyclohexane	Benzene	Ethyl Benzene	n-Tridecane
39	.25			.25	.5
40		.5		.25	.25
41		.25		.5	.25
42		.25		.25	.5
43		.25	.5	.25	
44	.4	.2		.2	.2
45	.2	.4		.2	.2
46	.2	.2		.4	.2
47	.2	.2		.2	.4
100	.1208	.8792			
101	.4064	.5936			
102	.6343	.3657			
103	.7074	.2926			
104	.9325	.0675			
105	.7085		.2915		
106	.4958		.5042		
107	.2618		.7382		
108	.0841		.9159		
109	.6905			.3095	
110	.3618			.6382	
111	.1473			.8527	
112	.8526				.1474
113	.5716				.4284
114	.1861				.8139
115		.6101	.3899		
116		.3962	.6038		
117		.2045	.7955		
118		.7791		.2209	
119		.3777		.6223	
120		.1240		.8760	
121		.8788			.1212
122		.6528			.3472
123		.3066			.6934
124			.7443	.2557	
125			.4457	.5543	
126			.2127	.7873	
127			.9005		.0995
128			.6734		.3266
129			.2906		.7094
130				.8508	.1492
131				.5847	.4153
132				.2697	.7303

APPENDIX B

DENSITIES OF MIXTURES

TABLE VII

DENSITIES OF MIXTURES

Mixture No.	(gm/cc) 25°C	45°C
n-Hexane	.6548	.6363
Cyclohexane	.7725	.7535
Benzene	.8729	.8517
Ethyl Benzene	.8623	.8450
n-Tridecane	.7528	.7385
1	.7381	.7196
2	.7076	.6892
3	.6800	.6617
4	.7991	.7793
5	.7407	.7214
6	.6934	.6745
7	.8093	.7926
8	.7568	.7397
9	.7049	.6872
10	.7388	.7244
11	.7203	.7053
12	.6942	.6780
13	.8398	.8195
14	.8126	.7925
15	.7903	.7707
16	.8401	.8226
17	.8196	.7990
18	.7940	.7759
19	.7538	.7394
20	.7563	.7412
21	.7610	.7447
22	.8638	.8458
23	.8658	.8469
24	.8686	.8487
25	.7634	.7488
26	.7802	.7646
27	.8096	.7919
28	.7672	.7526
29	.7874	.7721
30	.8164	.8002
31	.7321	.7146
32	.7616	.7436
33	.7855	.7678

TABLE VII (Continued)

Mixture No.	(gm/cc)	
	25° C	45° C
34	.7149	.6988
35	.7371	.7210
36	.7377	.7229
37	.7341	.7183
38	.7750	.7591
39	.7535	.7384
40	.7795	.7633
41	.7982	.7820
42	.7791	.7567
43	.8392	.8201
44	.7387	.7223
45	.7578	.7415
46	.7736	.7574
47	.7549	.7395
100	.7553	.7366
101	.7187	.7004
102	.6925	.6743
103	.6850	.6661
104	.6615	.6429
105	.7005	.6815
106	.7413	.7218
107	.7957	.7758
108	.8459	.8251
109	.7179	.6998
110	.7858	.7678
111	.8311	.8135
112	.6805	.6633
113	.7140	.6982
114	.7428	.7282
115	.8023	.7825
116	.8232	.8031
117	.8453	.8245
118	.7918	.7732
119	.8284	.8104
120	.8516	.8337
121	.7657	.7481
122	.7589	.7430
123	.7544	.7396
124	.8686	.8485
125	.8654	.8464
126	.8637	.8453
127	.8405	.8209
128	.7984	.7815
129	.7658	.7507
130	.8321	.8153
131	.7959	.7803
132	.7688	.7539

APPENDIX C

SONIC VELOCITY OF MIXTURES

TABLE VIII

SONIC VELOCITY OF MIXTURES

Mixture No.	Sonic Velocity m/sec 25° C	Sonic Velocity m/sec 45° C
n Hexane	1078.0	990.0
Cyclohexane	1264.0	1184.0
Benzene	1300.0	1196.0
Ethyl Benzene	1316.0	1228.0
n Tridecane	1295.0	1209.0
1	1204.9	1124.4
2	1156.5	1073.8
3	1114.8	1030.0
4	1211.8	1116.7
5	1150.3	1058.8
6	1106.8	1017.5
7	1255.3	1172.0
8	1194.4	1110.9
9	1133.4	1048.5
10	1264.7	1180.9
11	1224.7	1141.5
12	1167.0	1082.9
13	1270.1	1175.2
14	1255.1	1165.1
15	1253.0	1168.1
16	1295.5	1210.8
17	1275.5	1193.3
18	1262.9	1183.6
19	1283.0	1200.6
20	1272.3	1191.8
21	1261.8	1183.1
22	1310.3	1219.5
23	1304.9	1210.4
24	1300.7	1202.1
25	1282.6	1197.2
26	1271.8	1184.2
27	1267.7	1174.1
28	1290.7	1205.4
29	1290.9	1204.7
30	1295.8	1208.6
31	1172.0	1090.3
32	1214.4	1133.0
33	1232.3	1148.5
34	1195.6	1113.8

TABLE VIII (Continued)

Mixture No.	Sonic Velocity m/sec	
	25°C	45°C
35	1227.0	1147.1
36	1247.1	1166.5
37	1207.6	1124.7
38	1251.3	1134.0
39	1256.6	1172.3
40	1269.3	1188.2
41	1281.9	1197.8
42	1280.5	1197.1
43	1276.6	1186.3
44	1210.5	1127.7
45	1237.5	1156.7
46	1248.2	1165.4
47	1252.4	1169.8
100	1233.7	1153.8
101	1174.0	1092.7
102	1133.6	1050.5
103	1123.8	1036.6
104	1088.0	1000.2
105	1112.5	1022.7
106	1149.9	1057.6
107	1206.8	1111.5
108	1266.1	1165.1
109	1151.3	1064.2
110	1228.3	1139.9
111	1280.7	1192.5
112	1137.3	1050.9
113	1211.6	1125.7
114	1273.5	1188.0
115	1253.1	1165.7
116	1259.5	1167.9
117	1274.1	1176.2
118	1264.0	1182.9
119	1285.3	1200.6
120	1306.7	1218.1
121	1260.6	1181.0
122	1266.3	1186.2
123	1281.5	1198.1
124	1301.1	1201.7
125	1306.4	1211.4
126	1311.8	1219.2
127	1277.1	1178.0
128	1266.9	1175.7
129	1281.7	1194.2
130	1300.8	1212.5
131	1291.4	1204.8
132	1291.8	1205.2

APPENDIX D

SONIC VELOCITY OF BINARY MIXTURES FROM THE LITERATURE

TABLE IX

PER CENT DEVIATION OF THE METHODS FOR COMPUTING SONIC VELOCITIES AS COMPARED WITH LITERATURE VALUES OF SONIC VELOCITIES FOR BINARY MIXTURES

System	Temperature°C	Average Percent Error		
		Rao Method	Wada Method	Nomoto Method
Toluene-Pentane (21)	20	.52	.46	.39
n Heptane-n Pentane (21)	20	.45	.45	.19
Benzene-Cyclohexane (6)	30	.82	.87	.85
Benzene-n Heptane (6)	30	.20	.15	1.15
Benzene-Decalin (6)	30	.23	.23	.82
Benzene-Hexadecane (6)	30	.38	.31	1.92
Cyclohexane-n Heptane (6)	30	.60	.63	.14
Decalin-Cyclohexane (6)	30	.14	.11	.26
Decalin-Cyclohexane (6)	20	.23	.19	.30
Diphenyl Methane-n Hexane (24)	30	1.93	1.57	.38
Decalin-n Hexadecane (6)	30	.12	.06	.17
n Hexadecane-n Heptane (6)	30	.15	.16	.45
Decalin-n Heptane (6)	30	.63	.49	.24
Benzene-n Heptane (50)	25	.11	.15	.62
n-Hexadecane-n Heptane (29)	20	.32	.30	.06

APPENDIX E

PROPAGATION OF ERRORS

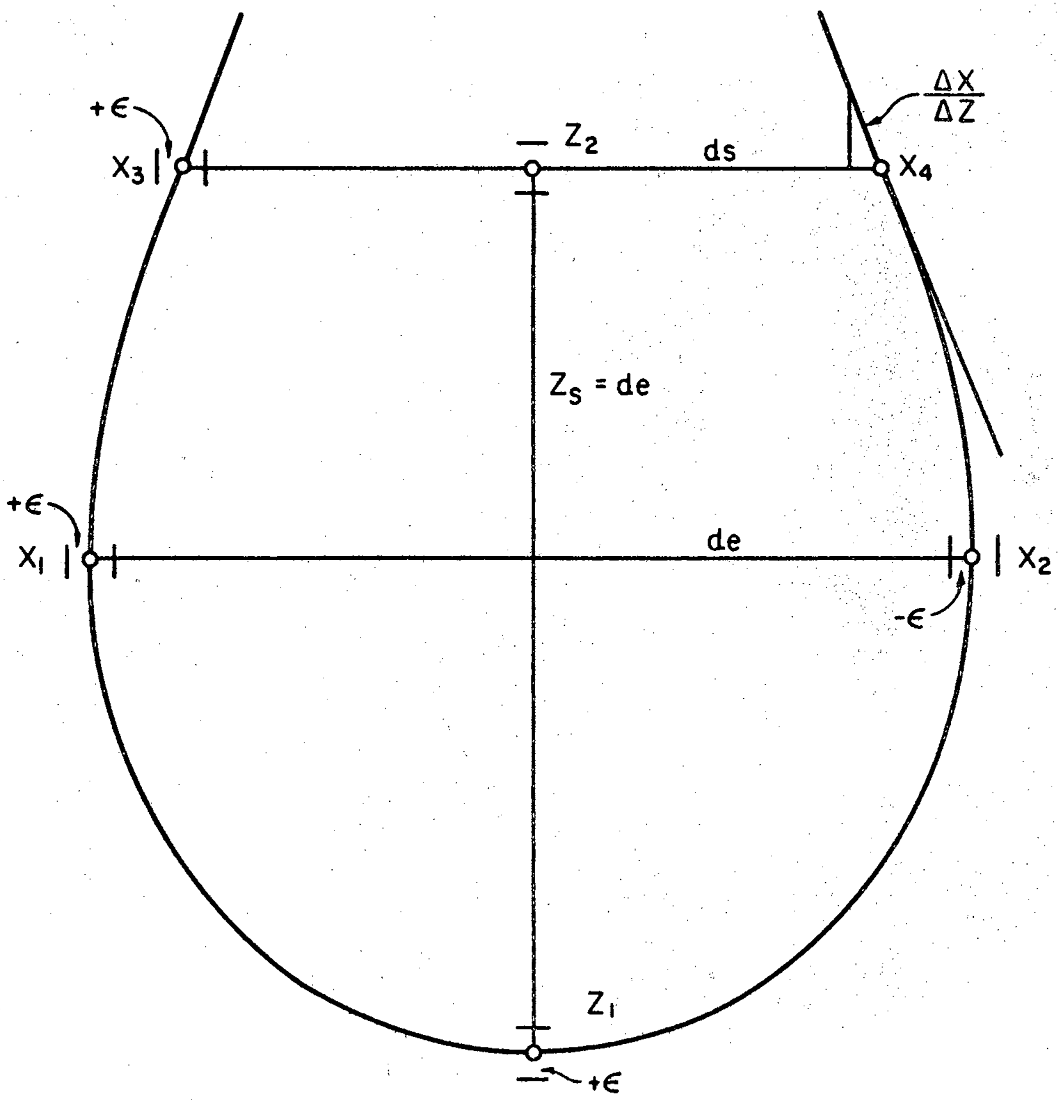

Figure 14. Pendant Drop, Showing Error of Measurement

PROPAGATION OF ERRORS

The most probable value of error in the surface tension as a result of uncertainties in the experimental measurements can be readily evaluated. First, consider the method of measuring the pendant drop and the relationship between the measured quantities and the surface tension. Figure 14 shows how the drop is measured and the possible effect of an error of ±ε in the comparator readings x_1, x_2, x_3, x_4, z_1, and z_2. Equation 117 presented by Stegemeier (47) can be used to estimate the surface tension.

$$\sigma = 0.3127\ g(\rho_L - \rho_V)\ \frac{d_e^{4.6444}}{d_s^{2.6444}} \tag{117}$$

The relationship between the comparator readings and the measured equatorial diameter is as follows:

$$d_e = x_2 - x_1 \tag{118}$$

The relationship between the selected plane diamter and the reading is given approximately by the following:

$$d_s = x_4 - x_3 - \left[2(z_1 + x_2 - x_1)\ \frac{\Delta x}{\Delta z} + C\right] \tag{119}$$

c is a constant. $\frac{\Delta x}{\Delta z}$ is the slope of the drop shape at the selected plane.

The constant c is chosen such that the term given below is equal to zero.

$$2(z_1+x_2-x_1)\frac{\Delta x}{\Delta z} + C = 0 \qquad (120)$$

The above term determines the error in the selected plane diameter when the incorrect plane is chosen. Thus the surface tension can be expressed in terms of the comparator readings as follows:

$$\sigma = \frac{0.3127\ g(\rho_V-\rho_L)(x_2-x_1)^{4.6444}}{x_4-x_3-2(z_1+x_2-x_1)\frac{\Delta x}{\Delta z} + C} \qquad (121)$$

The error in the surface tension as a result of an error in each of the comparator readings is given by the following when ϵ is the error in each of the comparator readings

$$\sigma_{x1} = \left(\frac{\partial\sigma}{\partial x_1}\right)\epsilon = -4.6444\frac{\sigma}{d_e}\ \epsilon + \frac{2.6444\left(\frac{2\Delta x}{\Delta z}\right)}{d_s}\ \epsilon \qquad (122)$$

$$\sigma_{x2} = \left(\frac{\partial\sigma}{\partial x_2}\right)\epsilon = 4.6444\frac{\sigma}{d_e}\ \epsilon - \frac{2.6444\sigma\left(\frac{2\Delta x}{\Delta z}\right)}{d_s}\ \epsilon \qquad (123)$$

$$\sigma_{x3} = \left(\frac{\partial\sigma}{\partial x_3}\right)\epsilon = 2.6444\frac{\sigma}{d_s}\ \epsilon \qquad (124)$$

$$\sigma_{x4} = \left(\frac{\partial\sigma}{\partial x_4}\right)\epsilon = -2.6444\frac{\sigma}{d_s}\ \epsilon \qquad (125)$$

$$\sigma_{z1} = \left(\frac{\partial\sigma}{\partial z_1}\right)\varepsilon = -2.6444\frac{\sigma}{d_s}\ (2)\ \left(\frac{\Delta x}{\Delta z}\right)\varepsilon \tag{126}$$

If we ignore errors in the gravitational constant, density difference, and the determination of the magnification factor, the most probable value of the error in the surface tension is expressed by:

$$\Delta\sigma = \sqrt{\sigma_{x1}^2 + \sigma_{x2}^2 + \sigma_{x3}^2 + \sigma_{x4}^2 + \sigma_{z1}^2} \tag{127}$$

The above equation was derived from Davies (8). Substituting equations (122 through 126) into 127 and using the relationship given below:

$$d_s = S\ d_e \tag{128}$$

Therefore:

$$\frac{\Delta\sigma}{\sigma} = \frac{\varepsilon}{d_e}\sqrt{\left(\frac{2.6444}{S}\right)^2 \left[2+3\left(\frac{2\Delta x}{\Delta z}\right)^2\right] \frac{-4(4.6444)(2.6444)\left(\frac{2\Delta x}{\Delta z}\right)}{S} + 2(4.6444)^2} \tag{129}$$

The slope $\frac{\Delta x}{\Delta z}$ can be determined from the results of Fordham (15) and Mills (30). This slope and the error in σ for a 1% error in the comparator readings are presented in Table X as a function of S.

TABLE X

PROBABLE ERROR IN SURFACE TENSION FOR A 1% ERROR IN COMPARATOR READINGS

S	$-\frac{\Delta x}{\Delta z}$	$\frac{\Delta\sigma}{\sigma}$ X 100%
.459	1.405	34.59
.502	1.248	29.35
.541	1.112	25.44
.576	0.993	22.45
.608	0.887	20.07
.639	0.801	18.23
.668	0.718	16.64
.695	0.643	15.32
.747	0.517	13.28
.773	0.456	12.40
.797	0.400	11.65
.844	0.297	10.38
.868	0.247	9.82
.891	0.199	9.32
.936	0.101	8.41
.959	0.055	8.02
.981	0.020	7.73

Percent error in comparator = $\frac{\epsilon}{d_e}$ X 100% = 1%

APPENDIX F

COMPARISON OF EXPERIMENTAL DATA WITH CALCULATED SURFACE TENSIONS FOR BINARY MIXTURES BY THE METHOD OF SPROW AND PRAUSNITZ (44)

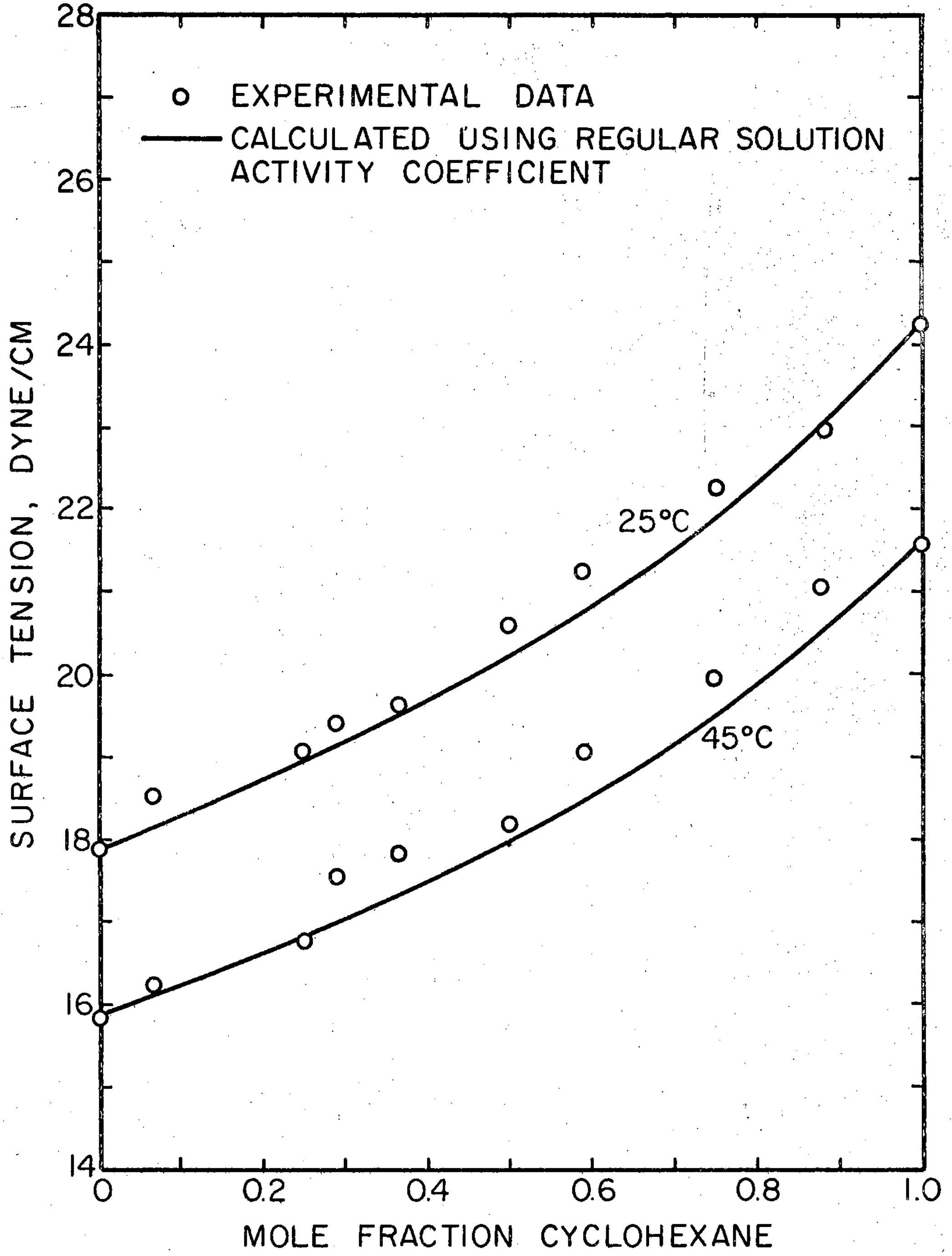

Figure 15. Effect of Composition on Surface Tension for the Hexane-Cyclohexane System. Experimental Data Compared with Calculated Surface Tension Values.

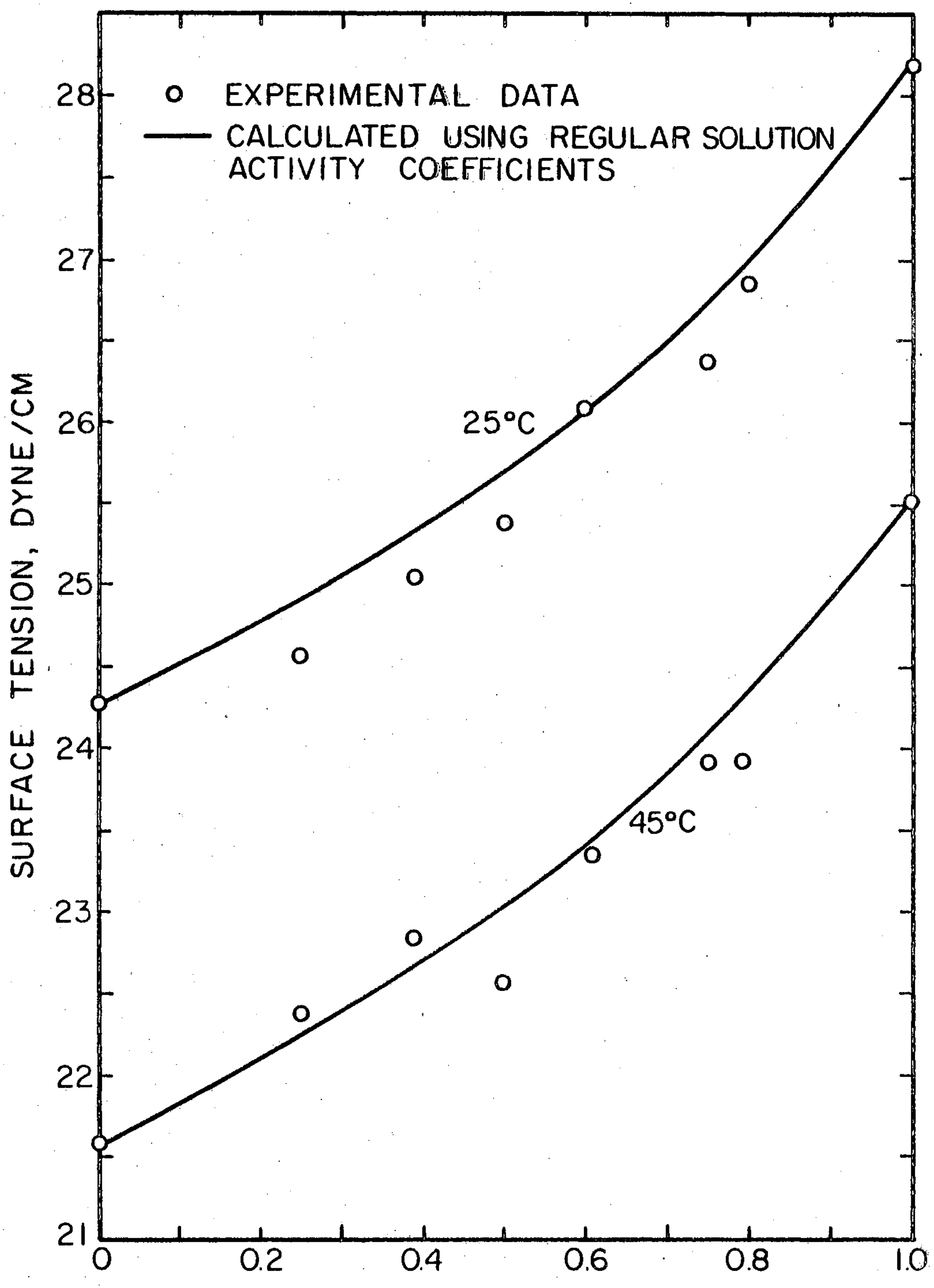

Figure 16. Effect of Composition on Surface Tension for the Benzene-Cyclohexane System. Experimental Data Compared with Calculated Surface Tension Values.

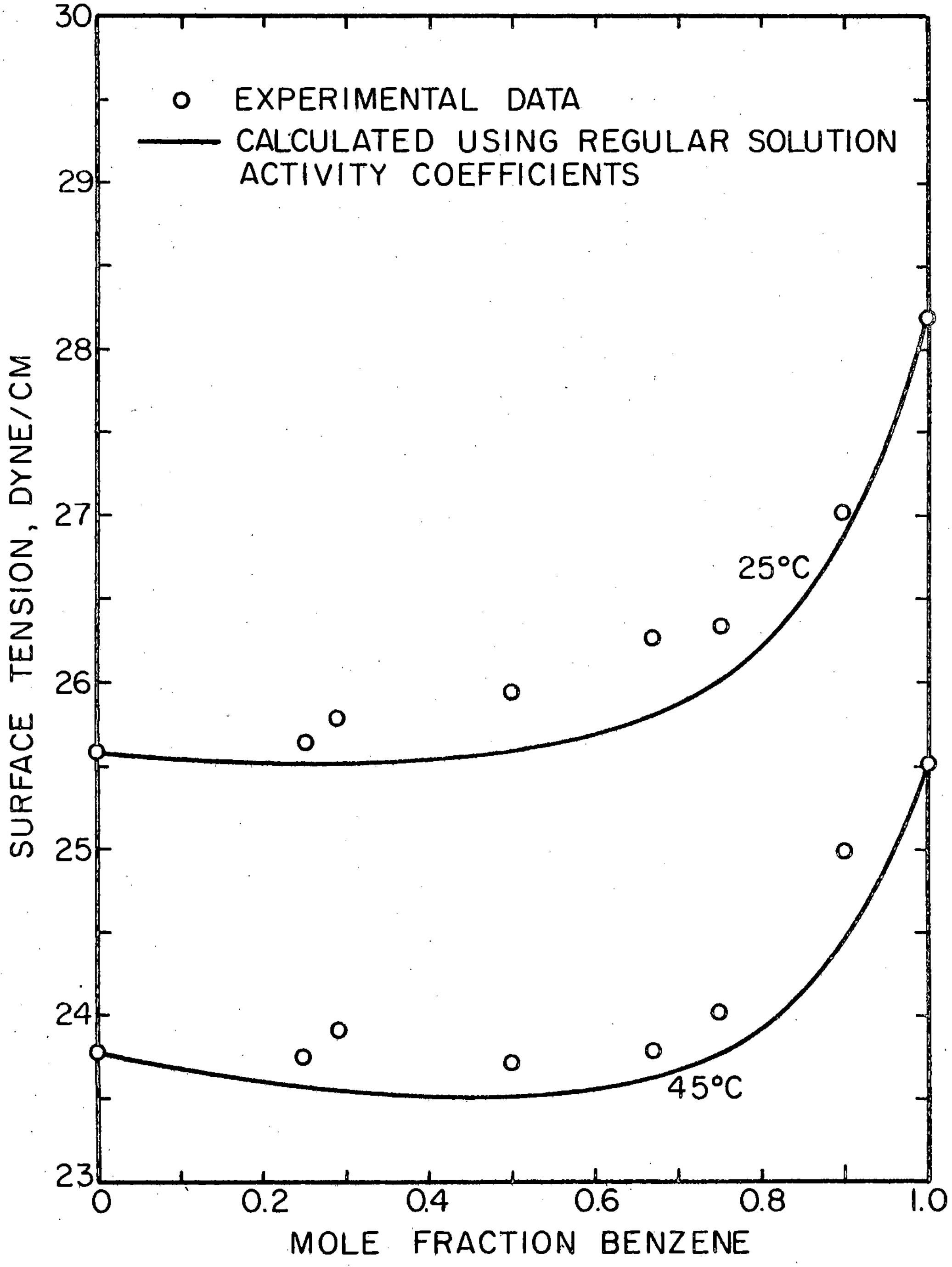

Figure 17. Effect of Composition on Surface Tension for the Benzene-Tridecane System. Experimental Data Compared with Calculated Surface Tension Values.

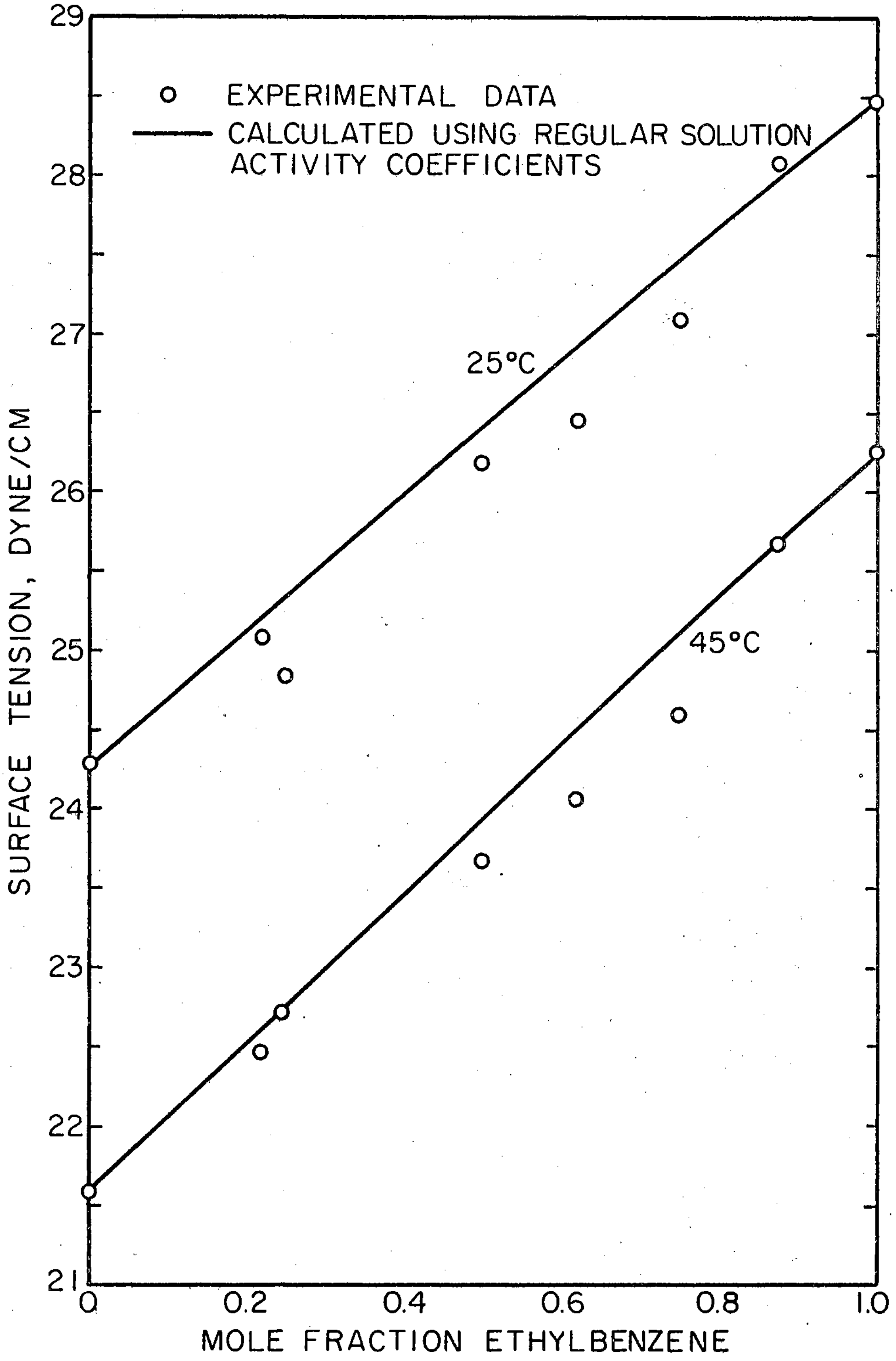

Figure 18. Effect of Composition on Surface Tension for the Ethylbenzene-Cyclohexane System. Experimental Data Compared with Calculated Surface Tension Values.

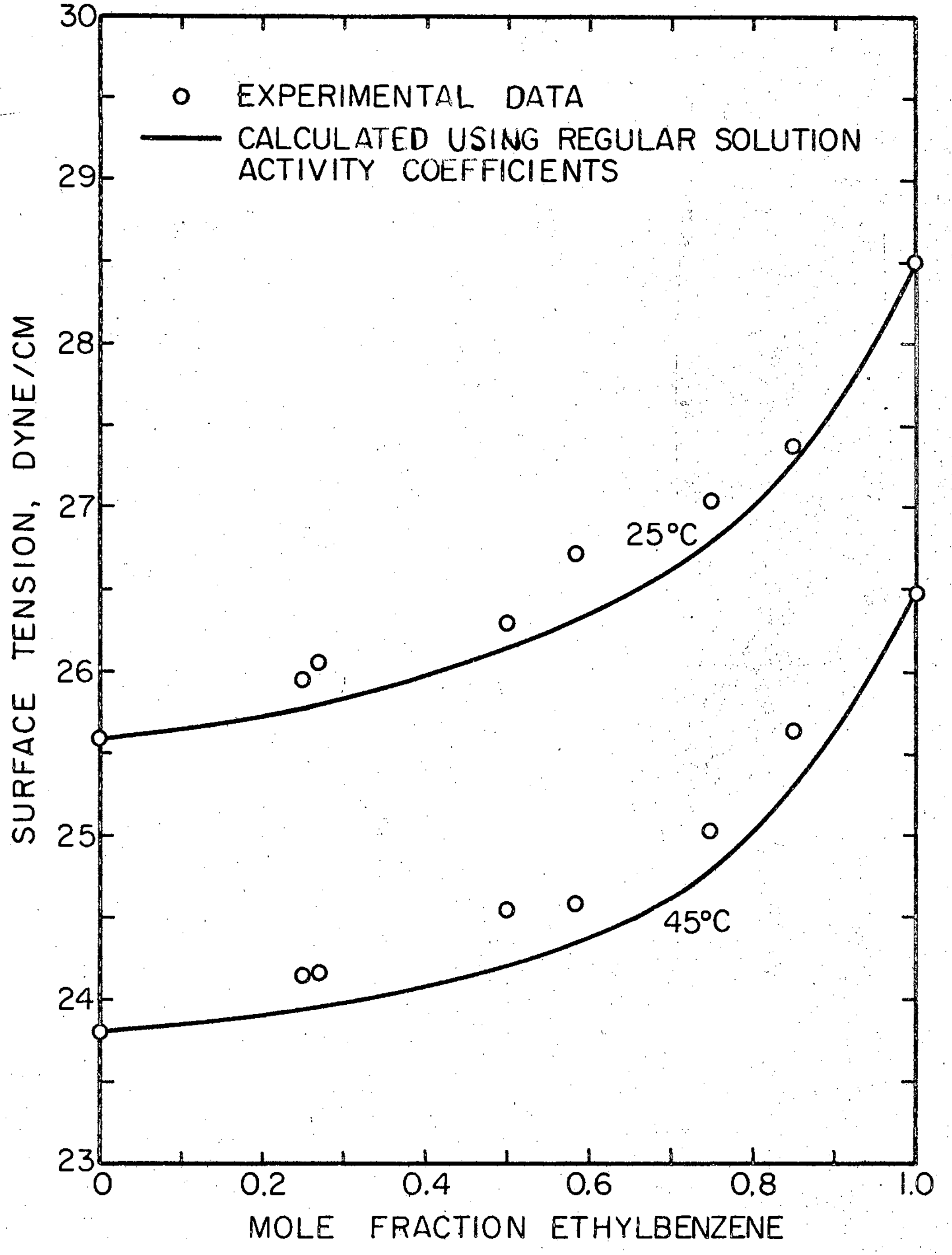

Figure 19. Effect of Composition on Surface Tension for the Ethylbenzene-Tridecane System. Experimental Data Compared with Calculated Surface Tension Values.

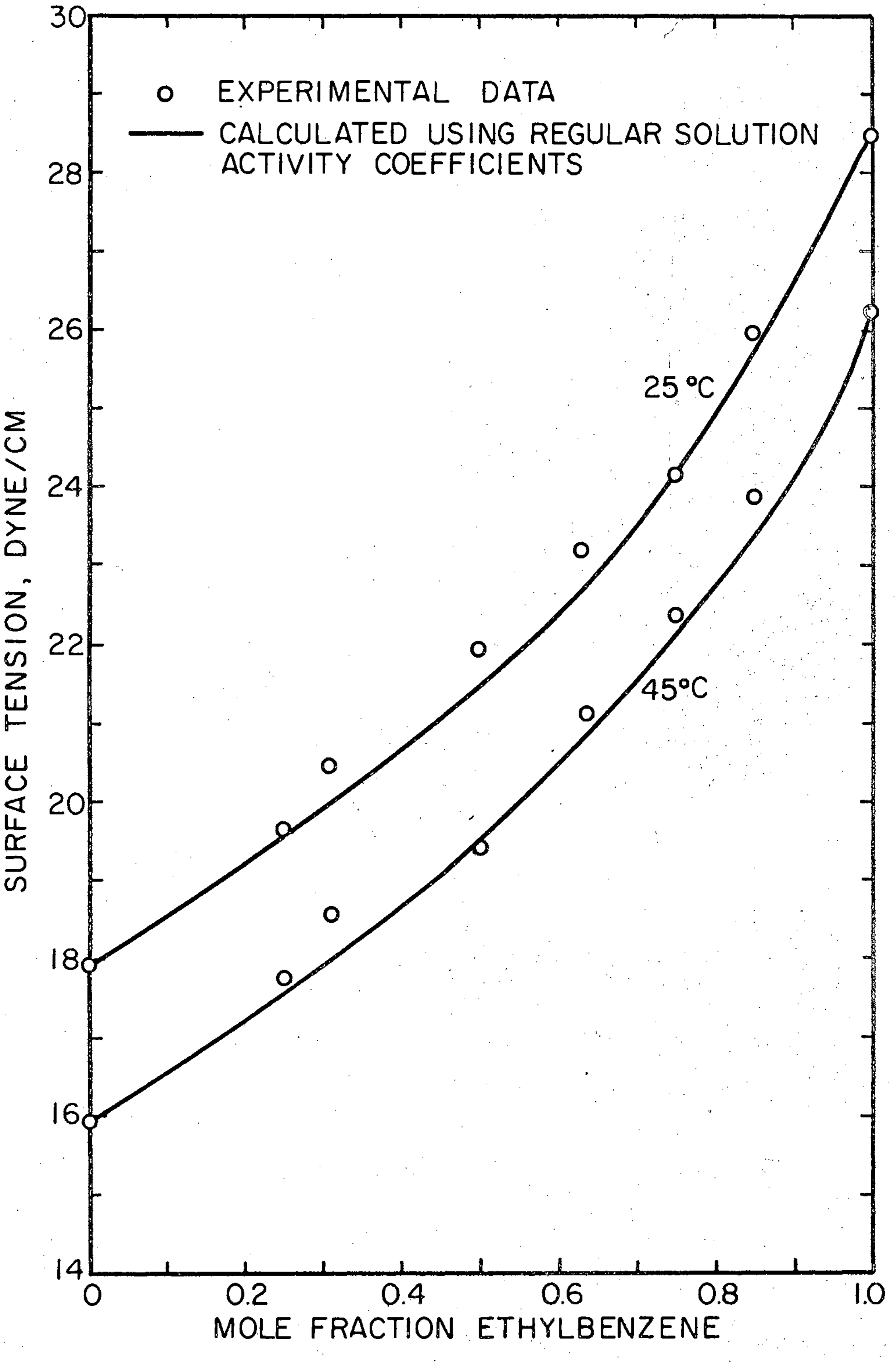

Figure 20. Effect of Composition on Surface Tension for the Ethylbenzene-N Hexane System. Experimental Data Compared with Calculated Surface Tension Values.

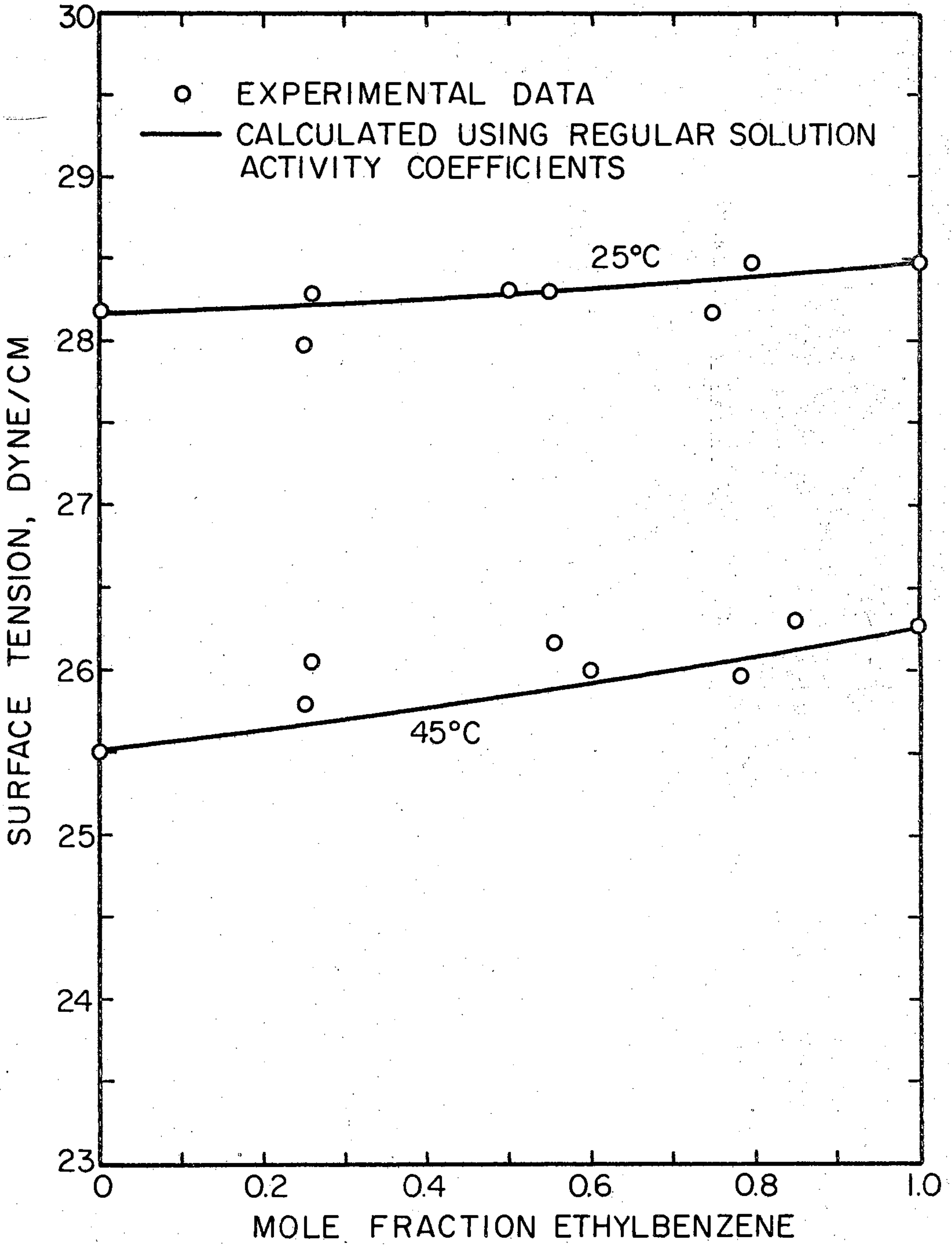

Figure 21. Effect of Composition on Surface Tension for the Ethylbenzene-Benzene System. Experimental Data Compared with Calculated Surface Tension Values.

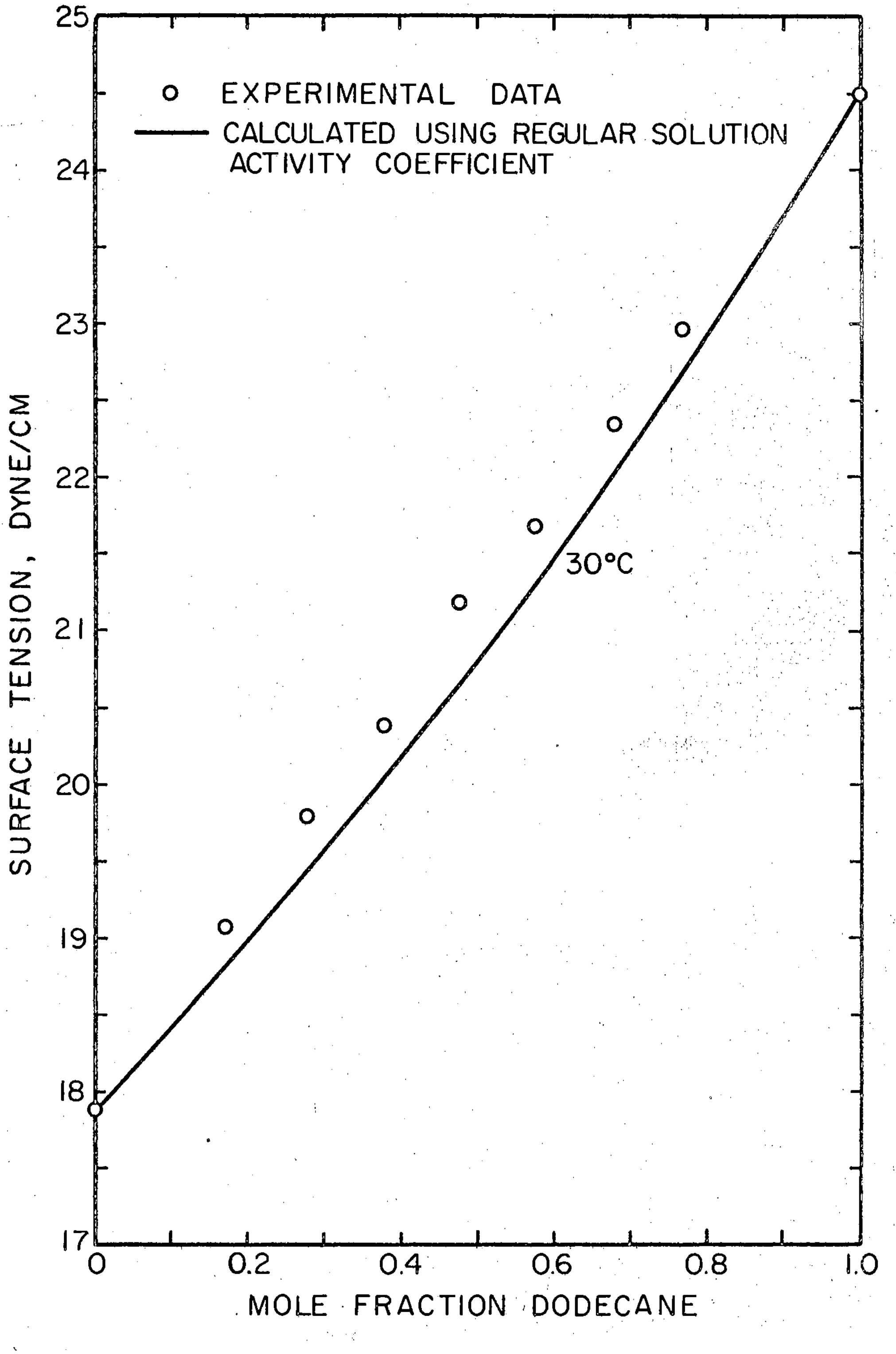

Figure 22. Effect of Composition on Surface Tension for the Isooctane-Dodecane System. Experimental Data Compared with Calculated Surface Tension Values.

APPENDIX G

DERIVATION OF THE RELATIONSHIP BETWEEN SURFACE TENSION AND POTENTIAL ENERGY FOR LIQUID MIXTURES

Consider a process in which a small amount of liquid from the bulk of a binary mixture is evaporated under equilibrium conditions. The composition of the vapor formed is given by the vapor-liquid equilibrium relationship:

$$Y_1 = K_1 X_1 \tag{130}$$

$$Y_2 = K_2 X_2 \tag{131}$$

Y_i is the vapor mole fraction and X_i is the bulk liquid composition. K_i is the vapor-liquid equilibrium constant. The energy required to increase the surface area to accommodate one mole of the evaporating molecules is given by equation 32.

$$\Omega \left(\frac{\partial u}{\partial A}\right)_T = \Omega \left[\sigma - T\left(\frac{\partial \sigma}{\partial T}\right)_A\right] \tag{132}$$

Ω is the surface area of one mole of evaporating molecules. σ is the surface tension of the mixture. The average surface area of the evaporating liquid is

$$\Omega = Y_1 \Omega_1 + Y_2 \Omega_2 \tag{133}$$

$$\Omega = K_1 X_1 \Omega_1 + K_2 X_2 \Omega_2 \tag{134}$$

Ω_i is the surface area of one mole of a pure component. As with equation 33, the energy required to bring the molecules to the surface is assumed to equal one half the energy to evaporate them:

$$\Phi^* = 2(K_1X_1\Omega_1 + K_2X_2\Omega_2)\left[\sigma - T\left(\frac{\partial\sigma}{\partial T}\right)_A\right] \tag{135}$$

Φ^* is the energy required to evaporate a small amount of liquid. The potential energy Φ_o, is the amount of energy required to evaporate a small amount of liquid from the bulk so that the vapor will have the same composition of the liquid. Φ_o is used to estimate sonic velocities and can be related to Φ^*. Φ^* is related to the enthalpy of the liquid and vapor by

$$\Phi^* = (H_V^* - H) \tag{136}$$

H_V^* is the enthalpy of a mixture in the vapor which is in equilibrium with the liquid. Also

$$\Phi^o = (H_V^o - H) \tag{137}$$

H_V^o is the enthalpy of a mixture in the vapor which has the same composition of the liquid. Combining equations 135, 136, and 137:

$$\Phi_o = (K_1X_1\Omega + K_2X_2\Omega_2)\left[\sigma - T\left(\frac{\partial\sigma}{\partial T}\right)_A\right] + (H_V^o - H_V^*) \tag{138}$$

VITA

2

Thomas Edwin Short, Jr.

Candidate for the Degree of

Doctor of Philosophy

Thesis: SURFACE TENSION AND SONIC VELOCITY IN MIXTURES OF HYDROCARBON LIQUIDS

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